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(54) Title: **PERSONAL CARE COMPOSITIONS COMPRISING A ZINC CONTAINING MATERIAL IN AN AQUEOUS SUR-
FACTANT COMPOSITION**

(57) Abstract: Disclosed are compositions comprising an effective amount of a zinc containing material having an aqueous solubil-
ity within the composition of less than about 25% by weight at 25°C; from about 5% to about 50% of a surfactant; and from about
40% to about 95% water; wherein the pH of the composition is greater than about 7. Further disclosed are compositions comprising
an effective amount of a zinc containing material having an aqueous solubility within the composition of less than about 25% by
weight at 25°C; from about 5% to about 50% of a surfactant; and from about 0.1% to about 5% of a zinc ionophoric material; from
about 40% to about 95% water; and wherein the pH of the composition is greater than about 7.

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PERSONAL CARE COMPOSITIONS COMPRISING A ZINC CONTAINING MATERIAL IN AN AQUEOUS SURFACTANT COMPOSITION

Field

Certain embodiments of the present invention relate to personal care compositions and methods of treating microbial and fungal infections on the skin or scalp. Additionally, certain embodiments of the present invention relate to methods for the treatment of dandruff and compositions which provide improved anti-dandruff activity.

Background

Of the trace metals, zinc is the second most abundant metal in the human body, catalyzing nearly every bio-process directly or indirectly through inclusion in many different metalloenzymes. The critical role zinc plays can be discerned from the symptoms of dietary deficiency, which include dermatitis, anorexia, alopecia and impaired overall growth. Zinc appears especially important to skin health and has been used (typically in the form of zinc oxide or calamine) for over 3000 years to control a variety of skin problems. Recent data more specifically points to the healing and repairing properties of topical zinc treatment to damaged skin, often resulting in increased rates of healing. There is a growing body of biochemical support for this phenomenon. Since dandruff has been previously shown to represent significant damage to scalp skin, topical zinc treatment could aid in the repair process.

Inorganic salts, such as zinc oxide, have been employed as bacteriostatic and/or fungistatic compounds in a large variety of products including paints, coatings and antiseptics. However, zinc salts do not possess as high of a level of biocidal efficacy as might be desired for many anti-dandruff and skin care applications.

While the prior art may have addressed some of the problems of chivying the use of inorganic salts in a large variety of products, they have not addressed the problems to the extent of or in the manner of the present invention. Therefore, there is a need for an improved personal care composition comprising a zinc containing material in an aqueous surfactant composition.

Summary

An embodiment of the present invention is directed to a composition comprising an effective amount of a zinc containing material having an aqueous solubility within the composition of less than about 25% by weight at 25°C; from about 5% to about 50% of a

surfactant; and from about 40% to about 95% water; wherein the pH of the composition is greater than about 7.

An additional embodiment of the present invention is directed to a composition comprising an effective amount of a zinc containing material having an aqueous solubility within the composition of less than about 25% by weight at 25°C; from about 5% to about 50% of a surfactant; and from about 0.1% to about 5% of a zinc ionophoric material; from about 40% to about 95% water; and wherein the pH of the composition is greater than about 7.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

Detailed Description

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

It has now surprisingly been found, in accordance with the present invention, that anti-dandruff efficacy can be dramatically increased in topical compositions by the use of polyvalent metal salts of pyrithione, such as zinc pyrithione, in combination with zinc containing material. Therefore an embodiment of the present invention provides topical compositions with improved benefits to the skin and scalp (e.g., improved antidandruff efficacy).

An embodiment of the present invention provides a stable composition for zinc containing material (e.g., zinc oxide) dispersion where the zinc containing material resides in a particulate form. It has been shown to be challenging to formulate aqueous systems containing a zinc containing material such as zinc oxide, due to their unique physical and chemical properties. They have a high density (i.e. 3 g/cm³), and needs to be evenly dispersed throughout the product so it will not aggregate or settle. They also have a very-reactive surface chemistry as well as the propensity to dissolve in systems with pH values below 7.5. This has provided a unique understanding concerning the need to control proton sources or other reactive/coordinating species (e.g., EDTA, citrate).

An embodiment of the present invention is directed toward a composition comprising an effective amount of a zinc containing material having an aqueous solubility within the composition of less than about 25% by weight at 25°C; from about

5% to about 50% of a surfactant; and from about 40% to about 95% water; wherein the pH of the composition is greater than about 7.

Another embodiment of the present invention is directed toward a composition comprising an effective amount of a zinc containing material having an aqueous solubility within the composition of less than about 25% by weight at 25°C; from about 5% to about 50% of a surfactant; and from about 0.1% to about 5% of a zinc ionophoric material; from about 40% to about 95% water; and wherein the pH of the composition is greater than about 7.

An embodiment of the present invention is directed toward a composition comprising labile zinc maintained by choice of an effective zinc containing material or formation of an effective zinc containing material in situ.

An embodiment of the present invention provides topical skin and/or hair compositions which provide superior benefits from zinc oxide. An embodiment of the present invention also provides a method for cleansing the hair and/or skin. These, and other benefits, will become readily apparent from the detailed description.

An embodiment of the present invention provides topical skin and/or hair compositions which provide superior benefits from zinc hydroxycarbonate. An embodiment of the present invention also provides a method for cleansing the hair and/or skin. These, and other benefits, will become readily apparent from the detailed description.

The present invention can comprise, consist of, or consist essentially of the essential elements and limitations of the invention described herein, as well any of the additional or optional ingredients, components, or limitations described herein.

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

The components and/or steps, including those which may optionally be added, of the various embodiments of the present invention, are described in detail below.

All documents cited are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention.

All ratios are weight ratios unless specifically stated otherwise.

All temperatures are in degrees Celsius, unless specifically stated otherwise.

Except as otherwise noted, all amounts including quantities, percentages, portions, and proportions, are understood to be modified by the word "about", and amounts are not intended to indicate significant digits.

Except as otherwise noted, the articles "a", "an", and "the" mean "one or more"

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of". The compositions and methods/processes of the present invention can comprise, consist of, and consist essentially of the essential elements and limitations of the invention described herein, as well as any of the additional or optional ingredients, components, steps, or limitations described herein.

Herein, "effective" means an amount of a subject active high enough to provide a significant positive modification of the condition to be treated. An effective amount of the subject active will vary with the particular condition being treated, the severity of the condition, the duration of the treatment, the nature of concurrent treatment, and like factors.

A. Zinc Containing Material

The composition of the present invention includes an effective amount of a zinc containing material. Herein "zinc containing material" or ZCM means a material comprising zinc bound covalently, and/or ionically, or physically by a host material.

Preferred embodiments of the present invention include an effective amount of a zinc containing material having an aqueous solubility within the composition of less than about 25%, by weight, at 25°C, more preferably less than about 20%; more preferably less than about 15%.

Preferred embodiments of the present invention include from 0.001% to 10% of a zinc containing material; more preferably from 0.01% to 5%; more preferably still from 0.1% to 3%.

In a preferred embodiment, the zinc containing material has an average particle size of from 100 nm to 30 μ m.

Examples of zinc containing materials useful in certain embodiments of the present invention include the following:

Inorganic Materials: Zinc aluminate, Zinc carbonate, Zinc oxide and materials containing zinc oxide (i.e., calamine), Zinc phosphates (i.e., orthophosphate and pyrophosphate), Zinc selenide, Zinc sulfide, Zinc silicates (i.e., ortho- and meta-zinc

silicates), Zinc silicofluoride, Zinc Borate, Zinc hydroxide and hydroxy sulfate, zinc-containing layered materials and combinations thereof.

Further, layered structures are those with crystal growth primarily occurring in two dimensions. It is conventional to describe layer structures as not only those in which all the atoms are incorporated in well-defined layers, but also those in which there are ions or molecules between the layers, called gallery ions (A.F. Wells "Structural Inorganic Chemistry" Clarendon Press, 1975). Zinc-containing layered materials (ZLM's) may have zinc incorporated in the layers and/or as more labile components of the gallery ions.

Many ZLM's occur naturally as minerals. Common examples include hydrozincite (zinc carbonate hydroxide), basic zinc carbonate, aurichalcite (zinc copper carbonate hydroxide), rosasite (copper zinc carbonate hydroxide) and many related minerals that are zinc-containing. Natural ZLM's can also occur wherein anionic layer species such as clay-type minerals (e.g., phyllosilicates) contain ion-exchanged zinc gallery ions. All of these natural materials can also be obtained synthetically or formed in situ in a composition or during a production process.

Another common class of ZLM's, which are often, but not always, synthetic, is layered doubly hydroxides, which are generally represented by the formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} A^{m-}_{x/m} \cdot nH_2O$ and some or all of the divalent ions (M^{2+}) would be represented as zinc ions (Crepaldi, EL, Pava, PC, Tronto, J, Valim, JB *J. Colloid Interfac. Sci.* **2002**, *248*, 429-42).

Yet another class of ZLM's can be prepared called hydroxy double salts (Morioka, H., Tagaya, H., Karasu, M, Kadokawa, J, Chiba, K *Inorg. Chem.* **1999**, *38*, 4211-6). Hydroxy double salts can be represented by the general formula $[M^{2+}_{1-x}M^{2+}_{1+x}(OH)_{3(1-y)}]^{x+} A^{n-}_{(1=3y)/n} \cdot nH_2O$ where the two metal ion may be different; if they are the same and represented by zinc, the formula simplifies to $[Zn_{1+x}(OH)_2]^{2x+} 2x A^- \cdot nH_2O$. This latter formula represents (where $x=0.4$) common materials such as zinc hydroxychloride and zinc hydroxynitrate. These are related to hydrozincite as well wherein the divalent anion is replaced by a monovalent anion. These materials can also be formed in situ in a composition or in or during a production process.

These classes of ZLM's represent relatively common examples of the general category and are not intended to be limiting as to the broader scope of materials which fit this definition.

Natural Zinc containing materials / Ores and Minerals: Sphalerite (zinc blende), Wurtzite, Smithsonite, Franklinite, Zincite, Willemite, Troostite, Hemimorphite and combinations thereof.

Organic Salts: Zinc fatty acid salts (i.e., caproate, laurate, oleate, stearate, etc.), Zinc salts of alkyl sulfonic acids, Zinc naphthenate, Zinc tartrate, Zinc tannate, Zinc phytate, Zinc monoglycerolate, Zinc allantoinate, Zinc urate, Zinc amino acid salts (i.e., methionate, phenylalanine, tryptophanate, cysteine, etc) and combinations thereof.

Polymeric Salts: Zinc polycarboxylates (i.e., polyacrylate), Zinc polysulfate and combinations thereof.

Physically Adsorbed Forms: Zinc-loaded ion exchange resins, Zinc adsorbed on particle surfaces, Composite particles in which zinc salts are incorporated, (i.e., as core/shell or aggregate morphologies) and combinations thereof.

Zinc Salts: zinc oxalate, zinc tannate, zinc tartrate, zinc citrate, zinc oxide, zinc carbonate, zinc hydroxide, zinc oleate, zinc phosphate, zinc silicate, zinc stearate, zinc sulfide, zinc undecylate, and the like, and mixtures thereof; preferably zinc oxide or zinc carbonate basic.

Commercially available sources of zinc oxide include Z-Cote and Z-Cote HPI (BASF), and USP I and USP II (Zinc Corporation of America).

Commercially available sources of zinc carbonate include Zinc Carbonate Basic (Cater Chemicals: Bensenville, IL, USA), Zinc Carbonate (Shepherd Chemicals: Norwood, OH, USA), Zinc Carbonate (CPS Union Corp.: New York, NY, USA), Zinc Carbonate (Elementis Pigments: Durham, UK), and Zinc Carbonate AC (Bruggemann Chemical: Newtown Square, PA, USA).

Zinc Salts That Become Insoluble Above a pH of 7: zinc acetate, zinc chloride, zinc bromide, zinc fluoride, zinc iodide, zinc sulfate, zinc citrate, zinc lactate, zinc nitrate, zinc propionate, zinc salicylate, zinc tartrate, zinc valerate, zinc gluconate, zinc selenate, zinc benzoate, zinc borate, zinc bromate, zinc formate, zinc glycerophosphate, zinc picrate, zinc butyrate, and the like, and combinations thereof.

Definition of ZCM Solubility: A zinc containing material with a solubility of less than 25% will have a measurable % soluble zinc value below a threshold value determined by the weight percent and molecular weight of the zinc compound. The

theoretical threshold value can be calculated by the following equation (see examples in the Table):

$$0.25 * \text{wt. \% Zn Compound in Composition} * \text{moles of Zinc in Compound} * 65.39 (\text{MW of Zn})$$

$$\text{MW of Zn Compound}$$

Zinc Compound	Formula	% Zn Compound In Composition	% soluble Zn ⁺² ; (if 25 wt.% of zinc source is soluble)*
Zinc Oxide	ZnO	1.0%	0.20%
Zinc Carbonate Basic (Hydrozincite)	Zn ₅ (CO ₃) ₂ (OH) ₆	1.0%	0.15%
Zinc Stearate	Zn(C ₁₈ H ₃₅ O ₂) ₂	1.0%	0.026%

B. Zinc Ionophoric Material (ZIM)

In another embodiment of the present invention, the composition further includes a zinc ionophoric material. Herein, "zinc ionophoric material" and "ZIM" means a material which is or forms a hydrophobic molecule capable of increasing cell permeability to zinc ions (i.e., exhibiting zinc ionophoric behavior). Without being bound by theory, it is believed that ZIMs shield the charge of the zinc ion to be transported, enabling it to penetrate the hydrophobic interior of the lipid bilayer. ZIMs may be channel-forming ionophores or mobile ion carriers. ZIMs may be those commonly known as zinc ionophores or those that are hydrophobic zinc chelators that possess zinc ionophoric behavior. Hydrophobic zinc chelators are materials that bind zinc and increase hydrophobicity of zinc ions such that, for example, it will partition into non-aqueous solvents. ZIMs can be effective including zinc being present in the composition or zinc being available within the system wherein a ZIM is present, yet preferred ZIMs contain zinc ions; i.e, zinc salt forms of materials exhibiting zinc ionophoric behavior.

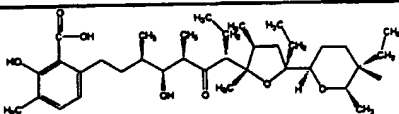
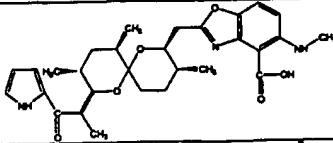
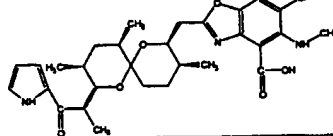
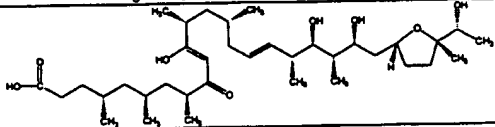
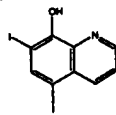
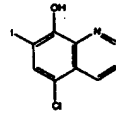
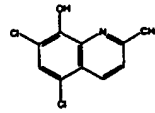
Preferred embodiments include from 0.01% to 5% of a ZIM; more preferably from 0.1% to 2%.

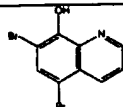
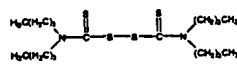
In embodiments having a zinc containing material and a ZIM, the ratio of zinc containing material to ZIM is preferably from 5:100 to 5:1; more preferably from about 2:10 to 3:1; more preferably still from 1:2 to 2:1.

In preferred embodiments of the present invention, the ZIM has a potency against target microorganisms such that the minimum inhibitory concentration ("MIC") is

below 5000 parts per million. The MIC is a measurement well understood by those skilled in the art and is indicative of anti-fungal efficacy. Generally, the lower the value of the composition, the better its anti-fungal efficacy, due to increased inherent ability of the anti-dandruff agent to inhibit the growth of microorganisms. The lowest tested dilution of anti-microbial active that yields no growth is defined as the MIC.

Examples of ZIMs useful in embodiments of the present invention include the following:

Class	Name (Synonyms)	Structure
Bio-molecules, Peptides and Naturally Occurring Materials and derivatives thereof having zinc ionophoric behavior	Lasalocid (X537A)	
	A23187 (Calcimycin)	
	4-Br A23187	
	Ionomycin	
	Cyclosporin A	Cyclic undecapeptide: cyclo-(MeBMT-Abu-Sar-MeLeu-Val-MeLeu-Ala-D-Ala-MeLeu-MeLeu-MeVal)
Hydroxyquinolines	Diodoquin (Iodoquinol; 5,7-Diiodo-8-hydroxyquinoline)	
	Enterovioform (Iodochloro hydroxyquinoline; 5-Cl, 7-I- 8-hydroxyquinoline)	
	Sterosan (Chloroquinaldol; 2-Me, 5,7-Dichloro-8-hydroxyquinoline)	

	5-7-Bibromo-8-hydroxyquinoline	
Sulfur-Based Compounds	Tetra-n-butyl thiuram Disulfide (TBTDS)	
Transport Enhancers	Albumin, histidine, arachidonic acid, picolinic acid, dihydroxyvitamin D ₃ , ethylmaltol	

In a preferred embodiment, the ZIM is pyrrhithione or a polyvalent metal salt of pyrrhithione. Any form of polyvalent metal pyrrhithione salts may be used, including platelet and needle structures. Preferred salts for use herein include those formed from the polyvalent metals magnesium, barium, bismuth, strontium, copper, zinc, cadmium, zirconium and mixtures thereof, more preferably zinc. Even more preferred for use herein is the zinc salt of 1-hydroxy-2-pyridinethione (known as "zinc pyrrhithione" or "ZPT"); more preferably ZPT in platelet particle form, wherein the particles have an average size of up to about 20 μ m, preferably up to about 5 μ m, more preferably up to about 2.5 μ m.

Pyridinethione anti-microbial and anti-dandruff agents are described, for example, in U.S. Pat. No. 2,809,971; U.S. Pat. No. 3,236,733; U.S. Pat. No. 3,753,196; U.S. Pat. No. 3,761,418; U.S. Pat. No. 4,345,080; U.S. Pat. No. 4,323,683; U.S. Pat. No. 4,379,753; and U.S. Pat. No. 4,470,982.

It is further contemplated that when ZPT is used as the anti-microbial particulate in the anti-microbial compositions herein, that an additional benefit of hair growth or re-growth may be stimulated or regulated, or both, or that hair loss may be reduced or inhibited, or that hair may appear thicker or fuller.

Zinc pyrrhithione may be made by reacting 1-hydroxy-2-pyridinethione (i.e., pyrrhithione acid) or a soluble salt thereof with a zinc salt (e.g. zinc sulfate) to form a zinc pyrrhithione precipitate, as illustrated in U.S. Patent No. 2,809,971.

C. Topical Carrier

In a preferred embodiment, the composition of the present invention is in the form of a topical compositions, which includes a topical carrier. Preferably, the topical carrier is selected from a broad range of traditional personal care carriers depending on the type of composition to be formed. By suitable selections of compatible carriers, it is contemplated that such a composition is prepared in the form of daily skin or hair products including conditioning treatments, cleansing products, such as hair and/or scalp shampoos, body washes, hand cleansers, water-less hand sanitizer/cleansers, facial cleansers and the like.

In a preferred embodiment, the carrier is water. Preferably the compositions of the present invention comprise from 40% to 95% water by weight of the composition; preferably from 50% to 85%, more preferably still from 60% to 80%.

D. Deterative Surfactant

The composition of the present invention includes a deterative surfactant. The deterative surfactant component is included to provide cleaning performance to the composition. The deterative surfactant component in turn comprises anionic deterative surfactant, zwitterionic or amphoteric deterative surfactant, or a combination thereof. Such surfactants should be physically and chemically compatible with the essential components described herein, or should not otherwise unduly impair product stability, aesthetics or performance.

Suitable anionic deterative surfactant components for use in the composition herein include those which are known for use in hair care or other personal care cleansing compositions. The concentration of the anionic surfactant component in the composition should be sufficient to provide the desired cleaning and lather performance, and generally range from about 5% to about 50%, preferably from about 8% to about 30%, more preferably from about 10% to about 25%, even more preferably from about 12% to about 22%.

Preferred anionic surfactants suitable for use in the compositions are the alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 8 to about 18 carbon atoms, x is an integer having a value of from 1 to 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium.

Preferably, R has from about 8 to about 18 carbon atoms, more preferably from about 10 to about 16 carbon atoms, even more preferably from about 12 to about 14 carbon atoms, in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be synthetic or they can be derived from fats, e.g., coconut oil, palm kernel oil, tallow. Lauryl alcohol and straight chain alcohols derived from coconut oil or palm kernel oil are preferred. Such alcohols are reacted with between about 0 and about 10, preferably from about 2 to about 5, more preferably about 3, molar proportions of ethylene oxide, and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Other suitable anionic deterative surfactants are the water-soluble salts of organic, sulfuric acid reaction products conforming to the formula $[R^1-SO_3-M]$ where R^1 is a straight or branched chain, saturated, aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is a cation described hereinbefore.

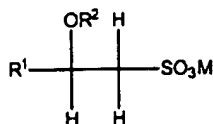
Still other suitable anionic deterative surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil or palm kernel oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil or palm kernel oil. Other similar anionic surfactants are described in U.S. Pat. Nos. 2,486,921; 2,486,922; and 2,396,278.

Other anionic deterative surfactants suitable for use in the compositions are the succinates, examples of which include disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; and dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic deterative surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock

and side reactions during the sulfonation process. A non limiting example of such an alpha-olefin sulfonate mixture is described in U.S. Patent 3,332,880.

Another class of anionic deterative surfactants suitable for use in the compositions are the beta-alkyloxy alkane sulfonates. These surfactants conform to the formula



where R¹ is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R² is a lower alkyl group having from about 1 to about 3 carbon atoms, preferably 1 carbon atom, and M is a water-soluble cation as described hereinbefore.

Preferred anionic deterative surfactants for use in the compositions include sodium lauryl sulfate, sodium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, ammonium lauryl sulfate, ammonium laureth sulfate, lauric monoglyceride sodium sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium cocoyl isethionate, and combinations thereof. Most preferred anionic deterative surfactants include sodium lauryl sulfate and sodium laureth sulfate.

Suitable amphoteric or zwitterionic deterative surfactants for use in the composition herein include those which are known for use in hair care or other personal care cleansing. Concentration of such amphoteric deterative surfactants preferably ranges from about 0.5% to about 20%, preferably from about 1% to about 10%. Non limiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Pat. Nos. 5,104,646 (Bolich Jr. et al.), 5,106,609 (Bolich Jr. et al.).

Amphoteric deterative surfactants suitable for use in the composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or

branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate. Preferred amphoteric deterative surfactants for use in the present invention include cocoamphoacetate, cocoamphodiacetate, lauroamphoacetate, lauroamphodiacetate, and mixtures thereof.

Zwitterionic deterative surfactants suitable for use in the composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. Zwitterionics such as betaines are preferred.

The compositions of the present invention may further comprise additional surfactants for use in combination with the anionic deterative surfactant component described hereinbefore. Suitable optional surfactants include nonionic and cationic surfactants. Any such surfactant known in the art for use in hair or personal care products may be used, provided that the optional additional surfactant is also chemically and physically compatible with the essential components of the composition, or does not otherwise unduly impair product performance, aesthetics or stability. The concentration of the optional additional surfactants in the composition may vary with the cleansing or lather performance desired, the optional surfactant selected, the desired product concentration, the presence of other components in the composition, and other factors well known in the art.

Non limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the compositions are described in McCutcheon's, Emulsifiers and Detergents, 2002 Annual, published by M. C. Publishing Co., and U.S. Pat. Nos. 3,929,678, 2,658,072; 2,438,091; 2,528,378.

E. Dispersed Particles

The composition of the present invention may include dispersed particles. In the compositions of the present invention, it is preferable to incorporate at least 0.025% by weight of the dispersed particles, more preferably at least 0.05%, still more preferably at least 0.1%, even more preferably at least 0.25%, and yet more preferably at least 0.5% by weight of the dispersed particles. In the compositions of the present invention, it is preferable to incorporate no more than about 20% by weight of the dispersed particles,

more preferably no more than about 10%, still more preferably no more than 5%, even more preferably no more than 3%, and yet more preferably no more than 2% by weight of the dispersed particles.

F. Aqueous Carrier

The compositions of the present invention are typically in the form of pourable liquids (under ambient conditions). The compositions will therefore typically comprise an aqueous carrier, which is present at a level of from about 20% to about 95%, preferably from about 60% to about 85%. The aqueous carrier may comprise water, or a miscible mixture of water and organic solvent, but preferably comprises water with minimal or no significant concentrations of organic solvent, except as otherwise incidentally incorporated into the composition as minor ingredients of other essential or optional components.

G. Additional Components

The compositions of the present invention may further comprise one or more optional components known for use in hair care or personal care products, provided that the optional components are physically and chemically compatible with the essential components described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Individual concentrations of such optional components may range from about 0.001% to about 10%.

Non-limiting examples of optional components for use in the composition include cationic polymers, conditioning agents (hydrocarbon oils, fatty esters, silicones), anti dandruff agents, suspending agents, viscosity modifiers, dyes, nonvolatile solvents or diluents (water soluble and insoluble), pearlescent aids, foam boosters, additional surfactants or nonionic cosurfactants, pediculocides, pH adjusting agents, perfumes, preservatives, chelants, proteins, skin active agents, sunscreens, UV absorbers, vitamins, minerals, herbal/fruit/food extracts, sphingolipids derivatives or synthetical derivative, and clay.

1. Cationic Polymers

The compositions of the present invention may contain a cationic polymer. Concentrations of the cationic polymer in the composition typically range from about 0.05% to about 3%, preferably from about 0.075% to about 2.0%, more preferably from about 0.1% to about 1.0%. Preferred cationic polymers will have cationic charge densities of at least about 0.9 meq/gm, preferably at least about 1.2 meq/gm, more

preferably at least about 1.5 meq/gm, but also preferably less than about 7 meq/gm, more preferably less than about 5 meq/gm, at the pH of intended use of the composition, which pH will generally range from about pH 3 to about pH 9, preferably between about pH 4 and about pH 8. Herein, "cationic charge density" of a polymer refers to the ratio of the number of positive charges on the polymer to the molecular weight of the polymer. The average molecular weight of such suitable cationic polymers will generally be between about 10,000 and 10 million, preferably between about 50,000 and about 5 million, more preferably between about 100,000 and about 3 million.

Suitable cationic polymers for use in the compositions of the present invention contain cationic nitrogen-containing moieties such as quaternary ammonium or cationic protonated amino moieties. The cationic protonated amines can be primary, secondary, or tertiary amines (preferably secondary or tertiary), depending upon the particular species and the selected pH of the composition. Any anionic counterions can be used in association with the cationic polymers so long as the polymers remain soluble in water, in the composition, or in a coacervate phase of the composition, and so long as the counterions are physically and chemically compatible with the essential components of the composition or do not otherwise unduly impair product performance, stability or aesthetics. Non limiting examples of such counterions include halides (e.g., chloride, fluoride, bromide, iodide), sulfate and methylsulfate.

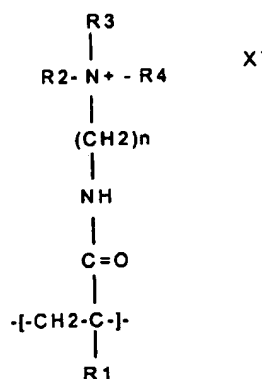
Non limiting examples of such polymers are described in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C. (1982)).

Non limiting examples of suitable cationic polymers include copolymers of vinyl monomers having cationic protonated amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone or vinyl pyrrolidone.

Suitable cationic protonated amino and quaternary ammonium monomers, for inclusion in the cationic polymers of the composition herein, include vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized

pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts.

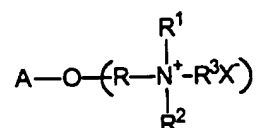
Other suitable cationic polymers for use in the compositions include copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer, copolymers of acrylamide and dimethyldiallylammonium chloride (referred to in the industry by CTFA as Polyquaternium 6 and Polyquaternium 7, respectively); amphoteric copolymers of acrylic acid including copolymers of acrylic acid and dimethyldiallylammonium chloride (referred to in the industry by CTFA as Polyquaternium 22), terpolymers of acrylic acid with dimethyldiallylammonium chloride and acrylamide (referred to in the industry by CTFA as Polyquaternium 39), and terpolymers of acrylic acid with methacrylamidopropyl trimethylammonium chloride and methylacrylate (referred to in the industry by CTFA as Polyquaternium 47). Preferred cationic substituted monomers are the cationic substituted dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, and combinations thereof. These preferred monomers conform to the formula



wherein R^1 is hydrogen, methyl or ethyl; each of R^2 , R^3 and R^4 are independently hydrogen or a short chain alkyl having from about 1 to about 8 carbon atoms, preferably from about 1 to about 5 carbon atoms, more preferably from about 1 to about 2 carbon atoms; n is an integer having a value of from about 1 to about 8, preferably from about 1 to about 4; and X is a counterion. The nitrogen attached to R^2 , R^3 and R^4 may be a protonated amine (primary, secondary or tertiary), but is preferably a quaternary

ammonium wherein each of R^2 , R^3 and R^4 are alkyl groups a non limiting example of which is polymethacrylamidopropyl trimonium chloride, available under the trade name Polycare 133, from Rhone-Poulenc, Cranberry, N.J., U.S.A.

Other suitable cationic polymers for use in the composition include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives. Suitable cationic polysaccharide polymers include those which conform to the formula



wherein A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual; R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof; R^1 , R^2 , and R^3 independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R^1 , R^2 and R^3) preferably being about 20 or less; and X is an anionic counterion as described in hereinbefore.

Preferred cationic cellulose polymers are salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10 and available from Amerchol Corp. (Edison, N.J., USA) in their Polymer LR, JR, and KG series of polymers. Other suitable types of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. under the tradename Polymer LM-200.

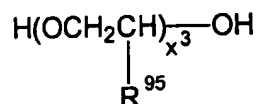
Other suitable cationic polymers include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride, specific examples of which include the Jaguar series commercially available from Rhone-Poulenc Incorporated and the N-Hance series commercially available from Aqualon Division of Hercules, Inc. Other suitable cationic polymers include quaternary nitrogen-containing cellulose ethers, some examples of which are described in U.S. Pat. No. 3,962,418. Other suitable cationic polymers include copolymers of etherified cellulose, guar and starch, some examples of which are described in U.S. Pat. No. 3,958,581. When used, the cationic polymers

herein are either soluble in the composition or are soluble in a complex coacervate phase in the composition formed by the cationic polymer and the anionic, amphoteric and/or zwitterionic deterative surfactant component described hereinbefore. Complex coacervates of the cationic polymer can also be formed with other charged materials in the composition.

Techniques for analysis of formation of complex coacervates are known in the art. For example, microscopic analyses of the compositions, at any chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the composition.

2. Nonionic polymers

Polyalkylene glycols having a molecular weight of more than about 1000 are useful herein. Useful are those having the following general formula:



wherein R^{95} is selected from the group consisting of H, methyl, and mixtures thereof. Polyethylene glycol polymers useful herein are PEG-2M (also known as Polyox WSR[®] N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M (also known as Polyox WSR[®] N-35 and Polyox WSR[®] N-80, available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M (also known as Polyox WSR[®] N-750 available from Union Carbide); PEG-9M (also known as Polyox WSR[®] N-3333 available from Union Carbide); and PEG-14 M (also known as Polyox WSR[®] N-3000 available from Union Carbide).

3. Conditioning agents

Conditioning agents include any material which is used to give a particular conditioning benefit to hair and/or skin. In hair treatment compositions, suitable conditioning agents are those which deliver one or more benefits relating to shine, softness, combability, antistatic properties, wet-handling, damage, manageability, body, and greasiness. The conditioning agents useful in the compositions of the present

invention typically comprise a water insoluble, water dispersible, non-volatile, liquid that forms emulsified, liquid particles. Suitable conditioning agents for use in the composition are those conditioning agents characterized generally as silicones (e.g., silicone oils, cationic silicones, silicone gums, high refractive silicones, and silicone resins), organic conditioning oils (e.g., hydrocarbon oils, polyolefins, and fatty esters) or combinations thereof, or those conditioning agents which otherwise form liquid, dispersed particles in the aqueous surfactant matrix herein. Such conditioning agents should be physically and chemically compatible with the essential components of the composition, and should not otherwise unduly impair product stability, aesthetics or performance.

The concentration of the conditioning agent in the composition should be sufficient to provide the desired conditioning benefits, and as will be apparent to one of ordinary skill in the art. Such concentration can vary with the conditioning agent, the conditioning performance desired, the average size of the conditioning agent particles, the type and concentration of other components, and other like factors.

1. Silicones

The conditioning agent of the compositions of the present invention is preferably an insoluble silicone conditioning agent. The silicone conditioning agent particles may comprise volatile silicone, non-volatile silicone, or combinations thereof. Preferred are non-volatile silicone conditioning agents. If volatile silicones are present, it will typically be incidental to their use as a solvent or carrier for commercially available forms of non-volatile silicone materials ingredients, such as silicone gums and resins. The silicone conditioning agent particles may comprise a silicone fluid conditioning agent and may also comprise other ingredients, such as a silicone resin to improve silicone fluid deposition efficiency or enhance glossiness of the hair.

The concentration of the silicone conditioning agent typically ranges from about 0.01% to about 10%, preferably from about 0.1% to about 8%, more preferably from about 0.1% to about 5%, more preferably from about 0.2% to about 3%. Non-limiting examples of suitable silicone conditioning agents, and optional suspending agents for the silicone, are described in U.S. Reissue Pat. No. 34,584, U.S. Pat. No. 5,104,646, and U.S. Pat. No. 5,106,609. The silicone conditioning agents for use in the compositions of the present invention preferably have a viscosity, as measured at 25°C, from about 20 to about 2,000,000 centistokes ("cSk"), more preferably from about 1,000 to about 1,800,000 cSk, even more preferably from about 50,000 to about 1,500,000

csk, more preferably from about 100,000 to about 1,500,000 csk.

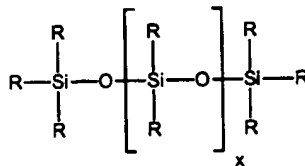
The dispersed silicone conditioning agent particles typically have a number average particle diameter ranging from about 0.01 μ m to about 50 μ m. For small particle application to hair, the number average particle diameters typically range from about 0.01 μ m to about 4 μ m, preferably from about 0.01 μ m to about 2 μ m, more preferably from about 0.01 μ m to about 0.5 μ m. For larger particle application to hair, the number average particle diameters typically range from about 4 μ m to about 50 μ m, preferably from about 6 μ m to about 30 μ m, more preferably from about 9 μ m to about 20 μ m, more preferably from about 12 μ m to about 18 μ m.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, are found in *Encyclopedia of Polymer Science and Engineering*, vol. 15, 2d ed., pp 204-308, John Wiley & Sons, Inc. (1989).

a. Silicone oils

Silicone fluids include silicone oils, which are flowable silicone materials having a viscosity, as measured at 25°C, less than 1,000,000 csk, preferably from about 5 csk to about 1,000,000 csk, more preferably from about 100 csk to about 600,000 csk. Suitable silicone oils for use in the compositions of the present invention include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, non-volatile silicone fluids having hair conditioning properties may also be used.

Silicone oils include polyalkyl or polyaryl siloxanes which conform to the following Formula (III):



wherein R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable R groups for use in the compositions of the present invention include, but are not limited to: alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkamino, and ether-substituted, hydroxyl-substituted, and

halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic amines and quaternary ammonium groups.

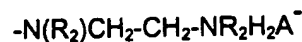
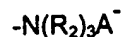
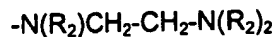
Preferred alkyl and alkenyl substituents are C₁ to C₅ alkyls and alkenyls, more preferably from C₁ to C₄, more preferably from C₁ to C₂. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains, and are preferably from C₁ to C₅, more preferably from C₁ to C₄, even more preferably from C₁ to C₃, more preferably from C₁ to C₂. As discussed above, the R substituents can also contain amino functionalities (e.g. alkamino groups), which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri- alkylamino and alkoxyamino groups, wherein the aliphatic portion chain length is preferably as described herein.

b. Amino and Cationic silicones

Cationic silicone fluids suitable for use in the compositions of the present invention include, but are not limited to, those which conform to the general formula (V):

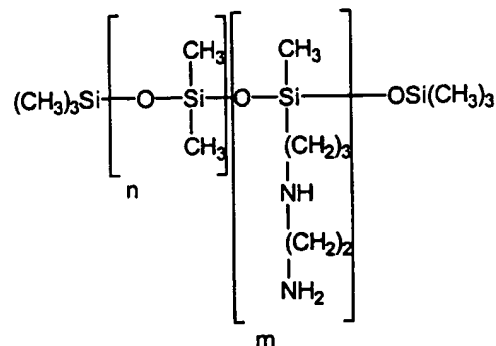


wherein G is hydrogen, phenyl, hydroxy, or C₁-C₈ alkyl, preferably methyl; a is 0 or an integer having a value from 1 to 3, preferably 0; b is 0 or 1, preferably 1; n is a number from 0 to 1,999, preferably from 49 to 499; m is an integer from 1 to 2,000, preferably from 1 to 10; the sum of n and m is a number from 1 to 2,000, preferably from 50 to 500; R₁ is a monovalent radical conforming to the general formula C_qH_{2q}L, wherein q is an integer having a value from 2 to 8 and L is selected from the following groups:

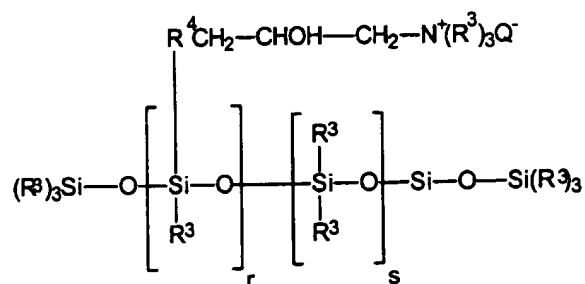


wherein R₂ is hydrogen, phenyl, benzyl, or a saturated hydrocarbon radical, preferably an alkyl radical from about C₁ to about C₂₀, and A⁺ is a halide ion.

An especially preferred cationic silicone corresponding to formula (V) is the polymer known as "trimethylsilylamodimethicone", which is shown below in formula (VI):



Other silicone cationic polymers which may be used in the compositions of the present invention are represented by the general formula (VII):



wherein R^3 is a monovalent hydrocarbon radical from C_1 to C_{18} , preferably an alkyl or alkenyl radical, such as methyl; R^4 is a hydrocarbon radical, preferably a C_1 to C_{18} alkylene radical or a C_{10} to C_{18} alkyleneoxy radical, more preferably a C_1 to C_8 alkyleneoxy radical; Q^- is a halide ion, preferably chloride; r is an average statistical value from 2 to 20, preferably from 2 to 8; s is an average statistical value from 20 to 200, preferably from 20 to 50. A preferred polymer of this class is known as UCARE SILICONE ALE 56™, available from Union Carbide.

c. Silicone gums

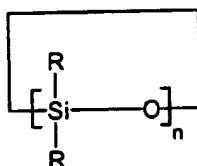
Other silicone fluids suitable for use in the compositions of the present invention are the insoluble silicone gums. These gums are polyorganosiloxane materials having a viscosity, as measured at 25°C , of greater than or equal to 1,000,000 csk. Silicone gums are described in U.S. Pat. No. 4,152,416; Noll and Walter, *Chemistry and Technology of Silicones*, New York: Academic Press (1968); and in General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. Specific non-

limiting examples of silicone gums for use in the compositions of the present invention include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

d. High refractive index silicones

Other non-volatile, insoluble silicone fluid conditioning agents that are suitable for use in the compositions of the present invention are those known as "high refractive index silicones," having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, more preferably at least about 1.55. The refractive index of the polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60. In this context, polysiloxane "fluid" includes oils as well as gums.

The high refractive index polysiloxane fluid includes those represented by general Formula (III) above, as well as cyclic polysiloxanes such as those represented by Formula (VIII) below:



wherein R is as defined above, and n is a number from about 3 to about 7, preferably from about 3 to about 5.

The high refractive index polysiloxane fluids contain an amount of aryl-containing R substituents sufficient to increase the refractive index to the desired level, which is described herein. Additionally, R and n must be selected so that the material is non-volatile.

Aryl-containing substituents include those which contain alicyclic and heterocyclic five and six member aryl rings and those which contain fused five or six member rings. The aryl rings themselves can be substituted or unsubstituted.

Generally, the high refractive index polysiloxane fluids will have a degree of aryl-containing substituents of at least about 15%, preferably at least about 20%, more preferably at least about 25%, even more preferably at least about 35%, more

preferably at least about 50%. Typically, the degree of aryl substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

Preferred high refractive index polysiloxane fluids have a combination of phenyl or phenyl derivative substituents (more preferably phenyl), with alkyl substituents, preferably C₁-C₄ alkyl (more preferably methyl), hydroxy, or C₁-C₄ alkylamino (especially -R¹NHR²NH₂ wherein each R¹ and R² independently is a C₁-C₃ alkyl, alkenyl, and/or alkoxy).

When high refractive index silicones are used in the compositions of the present invention, they are preferably used in solution with a spreading agent, such as a silicone resin or a surfactant, to reduce the surface tension by a sufficient amount to enhance spreading and thereby enhance the glossiness (subsequent to drying) of hair treated with the compositions.

Silicone fluids suitable for use in the compositions of the present invention are disclosed in U.S. Pat. No. 2,826,551, U.S. Pat. No. 3,964,500, U.S. Pat. No. 4,364,837, British Pat. No. 849,433, and *Silicon Compounds*, Petrarch Systems, Inc. (1984).

e. Silicone resins

Silicone resins may be included in the silicone conditioning agent of the compositions of the present invention. These resins are highly cross-linked polymeric siloxane systems. The cross-linking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system known to those of ordinary skill in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit (CH₃)₃SiO_{0.5}; D denotes the difunctional unit (CH₃)₂SiO; T denotes the trifunctional unit (CH₃)SiO_{1.5}; and Q denotes the quadra- or tetra-functional unit SiO₂. Primes of the unit symbols (e.g. M', D', T', and Q') denote substituents other than methyl, and must be specifically defined for each occurrence.

Preferred silicone resins for use in the compositions of the present invention include, but are not limited to MQ, MT, MTQ, MDT and MDTQ resins. Methyl is a preferred silicone substituent. Especially preferred silicone resins are MQ resins, wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular

weight of the silicone resin is from about 1000 to about 10,000.

The weight ratio of the non-volatile silicone fluid, having refractive index below 1.46, to the silicone resin component, when used, is preferably from about 4:1 to about 400:1, more preferably from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described herein. Insofar as the silicone resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e. the conditioning active, the sum of the fluid and resin should be included in determining the level of silicone conditioning agent in the composition.

2. Organic conditioning oils

The conditioning component of the compositions of the present invention may also comprise from about 0.05% to about 3%, preferably from about 0.08% to about 1.5%, more preferably from about 0.1% to about 1%, of at least one organic conditioning oil as the conditioning agent, either alone or in combination with other conditioning agents, such as the silicones (described herein).

a. Hydrocarbon oils

Suitable organic conditioning oils for use as conditioning agents in the compositions of the present invention include, but are not limited to, hydrocarbon oils having at least about 10 carbon atoms, such as cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated), including polymers and mixtures thereof. Straight chain hydrocarbon oils preferably are from about C₁₂ to about C₁₆. Branched chain hydrocarbon oils, including hydrocarbon polymers, typically will contain more than 19 carbon atoms.

Specific non-limiting examples of these hydrocarbon oils include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, polybutene, polydecene, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used, examples of which include highly branched, saturated or unsaturated, alkanes such as the permethyl-substituted isomers, e.g., the permethyl-substituted isomers of hexadecane and eicosane, such as 2, 2, 4, 4, 6, 6, 8, 8-dimethyl-10-methylundecane and 2, 2, 4, 4, 6, 6-dimethyl-8-methylnonane, available from

Permethyl Corporation. Hydrocarbon polymers such as polybutene and polydecene. A preferred hydrocarbon polymer is polybutene, such as the copolymer of isobutylene and butene. A commercially available material of this type is L-14 polybutene from Amoco Chemical Corporation. The concentration of such hydrocarbon oils in the composition preferably range from about 0.05% to about 20%, more preferably from about 0.08% to about 1.5%, and even more preferably from about 0.1% to about 1%.

b. Polyolefins

Organic conditioning oils for use in the compositions of the present invention can also include liquid polyolefins, more preferably liquid poly- α -olefins, more preferably hydrogenated liquid poly- α -olefins. Polyolefins for use herein are prepared by polymerization of C_4 to about C_{14} olefinic monomers, preferably from about C_6 to about C_{12} .

Non-limiting examples of olefinic monomers for use in preparing the polyolefin liquids herein include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, branched chain isomers such as 4-methyl-1-pentene, and mixtures thereof. Also suitable for preparing the polyolefin liquids are olefin-containing refinery feedstocks or effluents. Preferred hydrogenated α -olefin monomers include, but are not limited to: 1-hexene to 1-hexadecenes, 1-octene to 1-tetradecene, and mixtures thereof.

c. Fatty Esters

Other suitable organic conditioning oils for use as the conditioning agent in the compositions of the present invention include, but are not limited to, fatty esters having at least 10 carbon atoms. These fatty esters include esters with hydrocarbyl chains derived from fatty acids or alcohols (e.g. mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters). The hydrocarbyl radicals of the fatty esters hereof may include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

Specific examples of preferred fatty esters include, but are not limited to: isopropyl isostearate, hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, dihexyldecyl adipate, lauryl lactate, myristyl lactate, cetyl lactate, oleyl stearate, oleyl oleate, oleyl myristate, lauryl acetate, cetyl propionate, and oleyl adipate.

Other fatty esters suitable for use in the compositions of the present invention

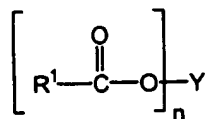
are mono-carboxylic acid esters of the general formula $R'COOR$, wherein R' and R are alkyl or alkenyl radicals, and the sum of carbon atoms in R' and R is at least 10, preferably at least 22.

Still other fatty esters suitable for use in the compositions of the present invention are di- and tri-alkyl and alkenyl esters of carboxylic acids, such as esters of C_4 to C_8 dicarboxylic acids (e.g. C_1 to C_{22} esters, preferably C_1 to C_6 , of succinic acid, glutaric acid, and adipic acid). Specific non-limiting examples of di- and tri- alkyl and alkenyl esters of carboxylic acids include isocetyl stearyl stearate, diisopropyl adipate, and tristearyl citrate.

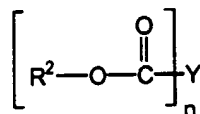
Other fatty esters suitable for use in the compositions of the present invention are those known as polyhydric alcohol esters. Such polyhydric alcohol esters include alkylene glycol esters, such as ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters.

Still other fatty esters suitable for use in the compositions of the present invention are glycerides, including, but not limited to, mono-, di-, and tri-glycerides, preferably di- and tri-glycerides, more preferably triglycerides. For use in the compositions described herein, the glycerides are preferably the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids, such as C_{10} to C_{22} carboxylic acids. A variety of these types of materials can be obtained from vegetable and animal fats and oils, such as castor oil, safflower oil, cottonseed oil, corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, lanolin and soybean oil. Synthetic oils include, but are not limited to, triolein and tristearin glyceryl dilaurate.

Other fatty esters suitable for use in the compositions of the present invention are water insoluble synthetic fatty esters. Some preferred synthetic esters conform to the general Formula (IX):



wherein R¹ is a C₇ to C₉ alkyl, alkenyl, hydroxyalkyl or hydroxyalkenyl group, preferably a saturated alkyl group, more preferably a saturated, linear, alkyl group; n is a positive integer having a value from 2 to 4, preferably 3; and Y is an alkyl, alkenyl, hydroxy or carboxy substituted alkyl or alkenyl, having from about 2 to about 20 carbon atoms, preferably from about 3 to about 14 carbon atoms. Other preferred synthetic esters conform to the general Formula (X):



wherein R² is a C₈ to C₁₀ alkyl, alkenyl, hydroxyalkyl or hydroxyalkenyl group; preferably a saturated alkyl group, more preferably a saturated, linear, alkyl group; n and Y are as defined above in Formula (X).

Specific non-limiting examples of suitable synthetic fatty esters for use in the compositions of the present invention include: P-43 (C₈-C₁₀ triester of trimethylolpropane), MCP-684 (tetraester of 3,3 diethanol-1,5 pentadiol), MCP 121 (C₈-C₁₀ diester of adipic acid), all of which are available from Mobil Chemical Company.

3. Other conditioning agents

Also suitable for use in the compositions herein are the conditioning agents described by the Procter & Gamble Company in U.S. Pat. Nos. 5,674,478, and 5,750,122. Also suitable for use herein are those conditioning agents described in U.S. Pat. Nos. 4,529,586 (Clairol), 4,507,280 (Clairol), 4,663,158 (Clairol), 4,197,865 (L'Oreal), 4,217, 914 (L'Oreal), 4,381,919 (L'Oreal), and 4,422, 853 (L'Oreal).

4. Additional Components

The compositions of the present invention may further include a variety of additional useful components. Preferred additional components include those discussed below:

1. Other Anti-Microbial Actives

The compositions of the present invention may further include one or more anti-fungal or anti-microbial actives in addition to the metal pyrithione salt actives. Suitable anti-microbial actives include coal tar, sulfur, whitfield's ointment, castellani's paint, aluminum chloride, gentian violet, octopirox (piroctone olamine), ciclopirox olamine, undecylenic acid and it's metal salts, potassium permanganate, selenium sulfide, sodium thiosulfate, propylene glycol, oil of bitter orange, urea preparations, griseofulvin, 8-

Hydroxyquinoline ciloquinol, thiobendazole, thiocarbamates, haloprogin, polyenes, hydroxypyridone, morpholine, benzylamine, allylamines (such as terbinafine), tea tree oil, clove leaf oil, coriander, palmarosa, berberine, thyme red, cinnamon oil, cinnamic aldehyde, citronellic acid, hinokitol, ichthyol pale, Sensiva SC-50, Elestab HP-100, azelaic acid, lyticase, iodopropynyl butylcarbamate (IPBC), isothiazalinones such as octyl isothiazalinone and azoles, and combinations thereof. Preferred anti-microbials include itraconazole, ketoconazole, selenium sulfide and coal tar.

a. Azoles

Azole anti-microbials include imidazoles such as benzimidazole, benzothiazole, bifonazole, butaconazole nitrate, climbazole, clotrimazole, croconazole, eberconazole, econazole, elubiol, fenticonazole, fluconazole, flutimazole, isoconazole, ketoconazole, lanconazole, metronidazole, miconazole, neticonazole, omoconazole, oxiconazole nitrate, sertaconazole, sulconazole nitrate, tioconazole, thiazole, and triazoles such as terconazole and itraconazole, and combinations thereof. When present in the composition, the azole anti-microbial active is included in an amount from about 0.01% to about 5%, preferably from about 0.1% to about 3%, and more preferably from about 0.3% to about 2%, by weight of the composition. Especially preferred herein is ketoconazole.

b. Selenium Sulfide

Selenium sulfide is a particulate anti-dandruff agent suitable for use in the anti-microbial compositions of the present invention, effective concentrations of which range from about 0.1% to about 4%, by weight of the composition, preferably from about 0.3% to about 2.5%, more preferably from about 0.5% to about 1.5%. Selenium sulfide is generally regarded as a compound having one mole of selenium and two moles of sulfur, although it may also be a cyclic structure that conforms to the general formula Se_xS_y , wherein $x + y = 8$. Average particle diameters for the selenium sulfide are typically less than $15\mu m$, as measured by forward laser light scattering device (e.g. Malvern 3600 instrument), preferably less than $10\mu m$. Selenium sulfide compounds are described, for example, in U.S. Pat. No. 2,694,668; U.S. Pat. No. 3,152,046; U.S. Pat. No. 4,089,945; and U.S. Pat. No. 4,885,107.

c. Sulfur

Sulfur may also be used as a particulate anti-microbial/anti-dandruff agent in the anti-microbial compositions of the present invention. Effective concentrations of the

particulate sulfur are typically from about 1% to about 4%, by weight of the composition, preferably from about 2% to about 4%.

d. Keratolytic Agents

The present invention may further comprise one or more keratolytic agents such as Salicylic Acid.

Additional anti-microbial actives of the present invention may include extracts of melaleuca (tea tree) and charcoal. The present invention may also comprise combinations of anti-microbial actives. Such combinations may include octopirox and zinc pyrithione combinations, pine tar and sulfur combinations, salicylic acid and zinc pyrithione combinations, octopirox and climbazole combinations, and salicylic acid and octopirox combinations, and mixtures thereof.

2. Hair loss prevention and Hair Growth Agents

The present invention may further comprise materials useful for hair loss prevention and hair growth stimulants or agents. Examples of such agents are Anti-Androgens such as Propecia, Dutasteride, RU5884; Anti-Inflammatories such as Glucocorticoids, Macrolides, Macrolides; Anti-Microbials such as Zinc pyrithione, Ketoconazole, Selenium sulfide, Acne Treatments; Immunosuppressives such as FK-506, Cyclosporin; vasodilators such as minoxidil, Aminexil® and combinations thereof.

3. Sensates

The present invention may further comprise topical sensate materials such as terpenes, vanilloids, alkyl amides, natural extracts and combinations thereof. Terpenes can include menthol and derivatives such as menthyl lactate, ethyl menthane carboxamide, and menthoxypropanediol. Other terpenes can include camphor, eucalyptol, carvone, thymol and combinations thereof. Vanilloids can include capsaicin, zingerone, eugenol, and vanillyl butyl ether. Alkyl amides can include spilanthal, hydroxy alpha-sanschool, pellitorine and combinations thereof. Natural extracts can include peppermint oil, eucalyptol, rosemary oil, ginger oil, clove oil, capsicum, jambu extract, cinnamon oil, linalyl and combinations thereof. Additional topical sensate materials can include methyl salicylate, anethole, benzocaine, lidocaine, phenol, benzyl nicotinate, nicotinic acid, cinnamic aldehyde, cinnamyl alcohol, piperine, and combinations thereof.

4. Humectant

The compositions of the present invention may contain a humectant. The humectants herein are selected from the group consisting of polyhydric alcohols, water soluble alkoxylated nonionic polymers, and mixtures thereof. The humectants, when

used herein, are preferably used at levels of from about 0.1% to about 20%, more preferably from about 0.5% to about 5%.

Polyhydric alcohols useful herein include glycerin, sorbitol, propylene glycol, butylene glycol, hexylene glycol, ethoxylated glucose, 1, 2-hexane diol, hexanetriol, dipropylene glycol, erythritol, trehalose, diglycerin, xylitol, maltitol, maltose, glucose, fructose, sodium chondroitin sulfate, sodium hyaluronate, sodium adenosine phosphate, sodium lactate, pyrrolidone carbonate, glucosamine, cyclodextrin, and mixtures thereof.

Water soluble alkoxylated nonionic polymers useful herein include polyethylene glycols and polypropylene glycols having a molecular weight of up to about 1000 such as those with CTFA names PEG-200, PEG-400, PEG-600, PEG-1000, and mixtures thereof.

5. Suspending Agent

The compositions of the present invention may further comprise a suspending agent at concentrations effective for suspending water-insoluble material in dispersed form in the compositions or for modifying the viscosity of the composition. Such concentrations range from about 0.1% to about 10%, preferably from about 0.3% to about 5.0%.

Suspending agents useful herein include polymeric suspending agents such as anionic polymers and nonionic polymers. Useful herein are vinyl polymers such as cross linked acrylic acid polymers with the CTFA name Carbomer, cellulose derivatives and modified cellulose polymers such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, nitro cellulose, sodium cellulose sulfate, sodium carboxymethyl cellulose, crystalline cellulose, cellulose powder, polyvinylpyrrolidone, polyvinyl alcohol, guar gum, hydroxypropyl guar gum, xanthan gum, arabia gum, tragacanth, galactan, carob gum, guar gum, karaya gum, carrageenin, pectin, agar, quince seed (*Cydonia oblonga* Mill), starch (rice, corn, potato, wheat), algae colloids (algae extract), microbiological polymers such as dextran, succinoglucan, pulleran, starch-based polymers such as carboxymethyl starch, methylhydroxypropyl starch, alginic acid-based polymers such as sodium alginate, alginic acid propylene glycol esters, acrylate polymers such as sodium polyacrylate, polyethylacrylate, polyacrylamide, polyethyleneimine, and inorganic water soluble material such as bentonite, aluminum magnesium silicate, laponite, hectonite, and anhydrous silicic acid.

Commercially available viscosity modifiers highly useful herein include Carbomers with tradenames Carbopol 934, Carbopol 940, Carbopol 950, Carbopol 980,

and Carbopol 981, all available from B. F. Goodrich Company, acrylates/steareth-20 methacrylate copolymer with tradename ACRYCOL 22 available from Rohm and Hass, nonoxynyl hydroxyethylcellulose with tradename AMERCELL POLYMER HM-1500 available from Amerchol, methylcellulose with tradename BENECEL, hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with tradename KLUCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF 67, all supplied by Hercules, ethylene oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.

Other optional suspending agents include crystalline suspending agents which can be categorized as acyl derivatives, long chain amine oxides, and mixtures thereof. These suspending agents are described in U.S. Pat. No. 4,741,855. These preferred suspending agents include ethylene glycol esters of fatty acids preferably having from about 16 to about 22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suitable suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate, etc.); long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate); and glyceryl esters (e.g., glyceryl distearate, trihydroxystearin, tribehenin) a commercial example of which is Thixin R available from Rheox, Inc. Long chain acyl derivatives, ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids in addition to the preferred materials listed above may be used as suspending agents.

Other long chain acyl derivatives suitable for use as suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na, K), particularly N,N-di(hydrogenated) C.sub.16, C.sub.18 and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Ill., USA).

Examples of suitable long chain amine oxides for use as suspending agents include alkyl dimethyl amine oxides, e.g., stearyl dimethyl amine oxide. Other suitable suspending agents include primary amines having a fatty alkyl moiety having at least about 16 carbon atoms, examples of which include palmitamine or

stearamine, and secondary amines having two fatty alkyl moieties each having at least about 12 carbon atoms, examples of which include dipalmitoylamine or di(hydrogenated tallow)amine. Still other suitable suspending agents include di(hydrogenated tallow)phthalic acid amide, and crosslinked maleic anhydride-methyl vinyl ether copolymer.

6. Other Optional Components

The compositions of the present invention may contain also vitamins and amino acids such as: water soluble vitamins such as vitamin B1, B2, B6, B12, C, pantothenic acid, pantothenyl ethyl ether, panthenol, biotin, and their derivatives, water soluble amino acids such as asparagine, alanin, indole, glutamic acid and their salts, water insoluble vitamins such as vitamin A, D, E, and their derivatives, water insoluble amino acids such as tyrosine, tryptamine, and their salts.

The compositions of the present invention may also contain pigment materials such as inorganic, nitroso, monoazo, disazo, carotenoid, triphenyl methane, triaryl methane, xanthene, quinoline, oxazine, azine, anthraquinone, indigoid, thionindigoid, quinacridone, phthalocianine, botanical, natural colors, including: water soluble components such as those having C. I. Names. The compositions of the present invention may also contain antimicrobial agents which are useful as cosmetic biocides and antidandruff agents including: water soluble components such as piroctone olamine, water insoluble components such as 3,4,4'- trichlorocarbanilide (triclocarban), triclosan and zinc pyrithione.

The compositions of the present invention may also contain chelating agents.

H. Coordinating Compound Having a Log Zn Binding Constant

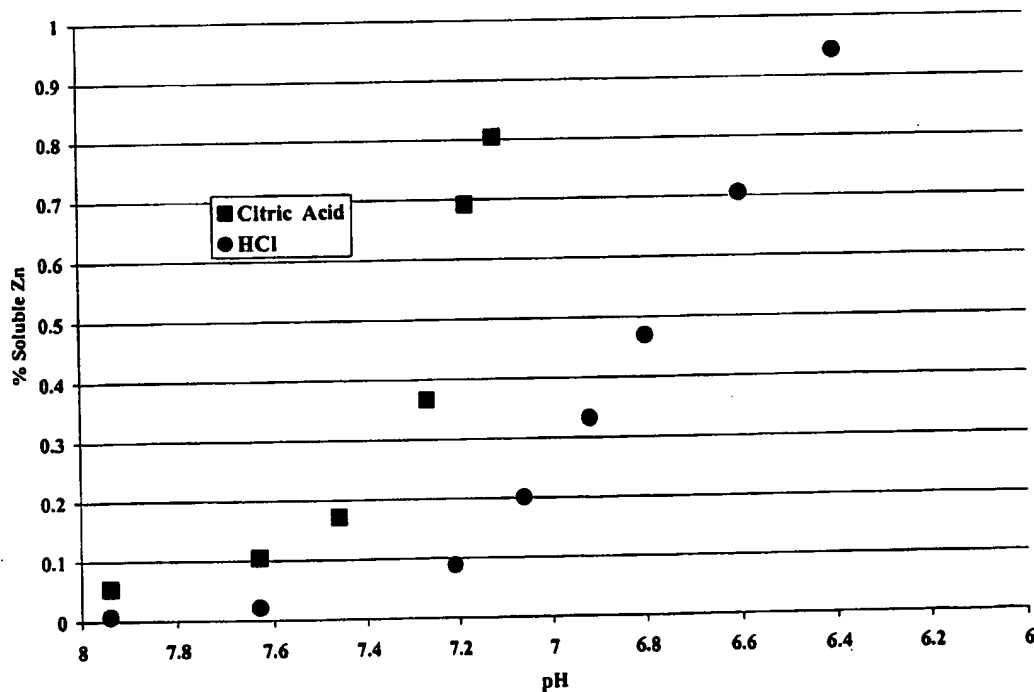
In an embodiment of the present invention, the composition further comprises a coordinating compound with a Log Zn binding constant in a range sufficient to maintain zinc bioavailability. Preferably, such a coordinating compound has a Log Zn binding constant less than about 6, preferably less than about 5, more preferable less than about 4, and greater than about -0.5. Preferably such a coordinating compound is an organic acid, strong mineral acid, or coordinating species. Preferred examples of such coordinating compounds include the following (respective Log Zn Binding Constant indicated in parenthesis): EDTA (16.5), EDDS (13.5), EDDA (11.1), NTA (10.7), Xylenol Orange (10.3), Cysteine (9.1), Cystine (6.7), Aspartic Acid (Aspartate) (5.9), Glycine (5.0), Citric Acid (Citrate) (4.8), Glutamic Acid (4.5), Methionine (4.4), Arginine

(4.2), Carbonic Acid (Carbonate) (3.9), Ornithine (3.8), Tatronic Acid (Tartrate) (3.2), Malic Acid (Malate) (2.9), Malonic Acid (Malonate) (2.9), Tartaric Acid (Tartrate) (2.7), Adipic Acid (Adipate) (2.6), Phosphoric Acid (Phosphate) (2.4), Phthalic Acid (Phthalate) (2.2), Glycolic Acid (Glycolate) (2.0), Lactic Acid (Lactate) (1.9), Succinic Acid (Succinate) (1.8), Acetic Acid (Acetate) (1.0), Sulfuric Acid (Sulfate) (0.9), Boric Acid (Borate) (0.9), Formic Acid (Formate) (0.6), Chloride (-0.3).

I. pH

In embodiments of the present invention, the pH may be in a range of from about 6.5 to about 12, preferably from about 6.7 to about 9, more preferably from about 6.8 to about 8.2, even more preferably from about 7.0 to about 8.0. In preferred embodiments, the pH of the present invention may be greater than about 6.5, more preferably greater than about 6.8, and still more preferably, greater than about 7.

In an embodiment of the present invention, the graph below demonstrates the relationship between pH and percent (%) soluble zinc. An acid level study is demonstrated wherein solubility and pH are measured in a composition. As the pH goes below 7.5, the % soluble zinc measured in a composition begins to rise. In the data below, citric acid appears to dissolve more zinc in the composition when compared to hydrochloric acid (HCl), on a weight basis.



comprises from 5% to 50% of a surfactant; a zinc containing material wherein zinc availability is measured by a zinc ion reacting with a metallochromic dye zincon to give a dye color change from orange to blue; and a zinc ionophore.

K. Method for Assessment of Zinc Lability in Zinc-Containing Products

Zinc lability is a measure of the chemical availability of zinc ion. Soluble zinc salts that do not complex with other species in solution have a relative zinc lability, by definition, of 100%. The use of partially soluble forms of zinc salts and/or incorporation in a matrix with potential complexants generally lowers the zinc lability substantially below the defined 100% maximum.

Zinc lability is assessed by combining a diluted zinc-containing solution or dispersion with the metallochromic dye xlenol orange (XO) and measurement of the degree of color change under specified conditions. The magnitude of color formation is proportional to the level of labile zinc. The procedure developed has been optimized for aqueous surfactant formulations but may be adapted to other physical product forms as well.

A spectrophotometer is used to quantify the color change at 572 nm, the wavelength of optimum color change for XO. The spectrophotometer is set to zero absorbance at 572nm utilizing a product control as close in composition to the test product except excluding the potentially labile form of zinc. The control and test products are then treated identically as follows. A 50 μ l product sample is dispensed into a jar and 95 ml of deaerated, distilled water are added and stirred. 5mL of a 23mg/mL xlenol orange stock solution at pH 5.0 is pipetted into the sample jar; this is considered time 0. The pH is then adjusted to 5. 50 ± 0.01 using dilute HCl or NaOH. After 10.0 minutes, a portion of the sample is filtered (0.45 μ) and the absorbance measured at 572nm. The measured absorbance is then compared to a separately measured control to determine the relative zinc lability (zero TO 100%). The 100% lability control is prepared in a matrix similar to the test products but utilizing a soluble zinc material (such as zinc sulfate) incorporated at an equivalent level on a zinc basis. The absorbance of the 100% lability control is measured as above for the test materials. The relative zinc lability is preferably greater than about 15%, more preferably greater than about 20%, and even more preferably greater than about 25%.

Using this methodology, the below examples demonstrate a material (hydrozincite) that has intrinsically high lability in an anionic surfactant system compared to one (ZnO) with low intrinsic lability. The examples further demonstrate that the low

lability of ZnO can be improved substantially by incorporating a protective material such as sodium bicarbonate, a source of carbonate anions and mixtures thereof:

	Relative Zinc Lability (%)	
	Simple Surfactant System ¹ Alone	Simple Surfactant System ¹ Plus Sodium Bicarbonate ²
Zinc Oxide	1.5	33.2
Hydrozincite	37.0	

¹Simple surfactant system: 6% sodium lauryl sulfate

²Addition of sodium bicarbonate: 0.2% level

L. Methods of Manufacture For Shampoo Compositions

The compositions of the present invention may be prepared by any known or otherwise effective technique, suitable for providing an anti-microbial composition provided that the resulting composition provides the excellent anti-microbial benefits described herein. Methods for preparing the anti-dandruff and conditioning shampoo embodiments of the present invention include conventional formulation and mixing techniques. A method such as that described in U.S. Pat. No. 5,837,661, could be employed, wherein the anti-microbial agent of the present invention would typically be added in the same step as the silicone premix is added in the U.S. Pat. No. 5,837,661 description.

M. Methods of Use

The compositions of the present invention may be used in direct application to the skin or in a conventional manner for cleansing skin and hair and controlling microbial infection (including fungal, viral, or bacterial infections) on the skin or scalp. The compositions herein are useful for cleansing the hair and scalp, and other areas of the body such as underarm, feet, and groin areas and for any other area of skin in need of treatment. The present invention may be used for treating or cleansing of the skin or hair of animals as well. An effective amount of the composition, typically from about 1g to about 50g, preferably from about 1g to about 20g of the composition, for cleansing hair, skin or other area of the body, is topically applied to the hair, skin or other area that has preferably been wetted, generally with water, and then rinsed off. Application to the hair typically includes working the shampoo composition through the hair.

A preferred method for providing anti-microbial (especially anti-dandruff) efficacy with a shampoo embodiment comprises the steps of: (a) wetting the hair with water, (b) applying an effective amount of the anti-microbial shampoo composition to the hair, and (c) rinsing the anti-microbial shampoo composition from the hair using water. These

steps may be repeated as many times as desired to achieve the cleansing, conditioning, and anti-microbial/anti-dandruff benefits sought.

It is also contemplated that when the anti-microbial active employed is zinc pyrithione, and/or if other optional hair growth regulating agents are employed, the anti-microbial compositions of the present invention, may, provide for the regulation of growth of the hair. The method of regularly using such shampoo compositions comprises repeating steps a, b, and c (above).

A further embodiment of the present invention comprises a method comprising the steps of (a) wetting the hair with water, (b) applying an effective amount of a shampoo composition comprising a zinc ionophore, (c) rinsing the shampoo compositions from the hair using water; (d) applying an effective amount of a conditioner composition comprising a zinc containing material according to the present invention; (e) rinsing the conditioner composition from the hair using water. In a further embodiment, this method could be conducted wherein steps d and b are reversed. In a further embodiment, steps b and d can vary and be a shampoo, hair lotions, hair sprays, hair tonics, conditioning treatments, gels, mousses and dressings, and the like. A preferred embodiment of the above mentioned method includes a shampoo composition comprising zinc pyrithione and a conditioner composition comprising zinc oxide.

A further embodiment of the present invention comprises a method of treating athlete's foot comprising the use of the composition according to the present invention, a method of treating microbial infections comprising the use of composition as described herein, method of improving the appearance of a scalp comprising the use of the composition according present invention, a method of treating fungal infections comprising the use of the composition according to the present invention, a method of treating dandruff comprising the use of the composition of the present invention, a method of treating diaper dermatitis and candidiasis comprising the use of the compositions of the present invention as described herein, a method of treating tinea capitis comprising the use of the composition according to the present invention, a method of treating yeast infections comprising the use of the composition according to the present invention, a method of treating onychomycosis comprising the use of the composition according to the present invention.

N. Examples

The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely

for the purpose of illustration, and are not to be construed as limitations of the present invention since many variations thereof are possible without departing from its scope.

The composition of the invention can be made by mixing one or more selected metal ion sources and one or more metal salts of pyrithione in an appropriate media or carrier, or by adding the individual components separately to the skin or hair cleansing compositions. Useful carriers are discussed more fully above.

1. Topical Compositions

All exemplified compositions can be prepared by conventional formulation and mixing techniques. Component amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components. As used herein, "minors" refers to those optional components such as preservatives, viscosity modifiers, pH modifiers, fragrances, foam boosters, and the like. As is apparent to one of ordinary skill in the art, the selection of these minors will vary depending on the physical and chemical characteristics of the particular ingredients selected to make the present invention as described herein. Other modifications can be undertaken by the skilled artisan without departing from the spirit and scope of this invention. These exemplified embodiments of the anti-microbial shampoo, anti-microbial cleansing compositions, anti-microbial cleansing /facial compositions of the present invention provide excellent anti-microbial efficacy.

Antimicrobial Shampoo – Examples 1-54

A suitable method for preparing the anti-microbial shampoo compositions described in Examples 1-54(below) follows:

About one-third to all of the sodium laureth sulfate (added as 25wt% solution) and acid are added to a jacketed mix tank and heated to about 60°C to about 80°C with slow agitation to form a surfactant solution. The pH of this solution is about 7.5. Sodium benzoate, Cocoamide MEA and fatty alcohols, (where applicable), are added to the tank and allowed to disperse. Ethylene glycol distearate ("EGDS") is added to the mixing vessel and allowed to melt (where applicable). After the EGDS is melted and dispersed, Kathon CG is added to the surfactant solution. The resulting mixture is cooled to about 25°C to about 40°C and collected in a finishing tank. As a result of this cooling step, the EGDS crystallizes to form a crystalline network in the product (where applicable). The remainder of the sodium laureth sulfate and other components, including the silicone and anti-microbial agent(s), are added to the finishing tank with agitation to ensure a

homogeneous mixture. Polymers (cationic or nonionic) are dispersed in water or oils as an about 0.1% to about 10% dispersion and/or solution and then added to the final mix. ZnO or Zinc Hydroxy carbonate ("ZHC") can be added to a premix of surfactants or water with or without the aid of a dispersing agent via conventional powder incorporation and mixing techniques into the final mix. Adjustment of ZnO particle size can be affected by various conventional mixing techniques obvious to one skilled in the art. Once all components have been added, additional viscosity modifiers may be added, as needed, to the mixture to adjust product viscosity to the extent desired.

Shampoo Compositions - Examples 1-10

Components	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Sodium Laureth Sulfate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Sodium Lauryl Sulfate	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Cocamidopropyl Betaine										
Sodium Cocoisethionate										
EGDS	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
CMEA	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	1.600
Cetyl Alcohol	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600
Guar Hydroxy Propyl Trimonium Chloride (1)	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500
Guar Hydroxy Propyl Trimonium Chloride (2)										
Guar Hydroxy Propyl Trimonium Chloride (3)										
Polyquaterium-10 (4)										
Polyquaterium-10 (5)										
PEG-7M (6)										
PEG-14M (7)										
PEG-45M (8)										
Dimethicone (9)	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Dimethicone (10)										
ZPT (11)	1.00	2.00	2.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Zinc Oxide	1.20	1.20	0.60	0.60	0.30	1.20	1.20	1.20	1.20	1.20
Zinc Hydroxy Carbonate										
Sodium Bicarbonate	0.20	0.20	0.20	0.20	0.20	0.10	0.05	0.25		0.20
Hydrochloric Acid	0.78	0.78	0.78	0.78	0.78	0.53	0.40	0.91	0.28	0.78
Magnesium Sulfate	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Sodium Chloride	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800
Sodium Xylenesulfonate										
Perfume	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750
Sodium Benzoate	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250
Kathon	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Benzyl Alcohol	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.

% Maximum XO Lability	63.2%					38.9%	38.5%	63.9%	23.5%	88.8%
% Soluble Zinc	0.024					0.017		2.55×10^{-3}	5.01×10^{-3}	0.011

- (1) Guar having a molecular weight of about 400,000, and having a charge density of about 0.84 meq/g, available from Aqualon.
 (2) Guar having a molecular weight of about 400,000, and having a charge density of about 2.0 meq/g, available from Aqualon.
 (3) Cationic guar Jaguar C17 available from Rhodia
 (4) Polymer JR30M available from Amerchol
 (5) Polymer LR400 available from Amerchol
 (6) Polyox WSR N-750 available from Amerchol
 (7) Polyox WSR N-3000 available from Amerchol
 (8) Polyox WSR N-60K available from Amerchol
 (9) Viscasil 330M available from General Electric Silicones
 (10) DC1664 available from Dow Corning Silicones
 (11) ZPT having an average particle size of about 2.5µm, available from Arch/Olin.

Shampoo Compositions - Examples 11-20

Components	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
Sodium Laureth Sulfate	10.00	10.00	10.00	10.00	10.00	12.50	10.00	10.00	10.00	10.00
Sodium Lauryl Sulfate	6.00	6.00	6.00	6.00	6.00	1.50	6.00	6.00	6.00	6.00
Cocamidopropyl Betaine					2.00	2.70				
Sodium Cocoisethionate										
EGDS	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
CMEA	1.600	0.800	0.800	1.600	0.800	0.800	0.800	0.800	0.800	0.800
Cetyl Alcohol	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600
Guar Hydroxy Propyl Trimonium Chloride (1)		0.500	0.500	0.500	0.500	0.500		0.500	0.500	0.500
Guar Hydroxy Propyl Trimonium Chloride (2)							0.500			
Guar Hydroxy Propyl Trimonium Chloride (3)	0.500									
Polyquaterium-10 (4)										
Polyquaterium-10 (5)										
PEG-7M (6)		0.200		0.200						
PEG-14M (7)										
PEG-45M (8)			0.200							
Dimethicone (9)	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Dimethicone (10)										
ZPT (11)	1.00	1.00	1.00	1.00	1.00	1.00	1.00			
Zinc Oxide	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20	0.60	0.30
Zinc Hydroxy Carbonate										
Sodium Bicarbonate	0.20	0.20	0.20	0.20	0.20	0.20	0.20			
Hydrochloric Acid	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.28	0.28	0.28
Magnesium Sulfate	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Sodium Chloride	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800
Sodium Xylenesulfonate										
Perfume	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750
Sodium Benzoate	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250
Kathon	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Benzyl Alcohol	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
% Maximum XO Lability		59.8%	58.2%	72.9%	71.7%		67.2%			
% Soluble Zinc										

- (1) Guar having a molecular weight of about 400,000, and having a charge density of about 0.84 meq/g, available from Aqualon.
 (2) Guar having a molecular weight of about 400,000, and having a charge density of about 2.0 meq/g, available from Aqualon.
 (3) Cationic guar Jaguar C17 available from Rhodia
 (4) Polymer JR30M available from Amerchol

- (5) Polymer LR400 available from Amerchol
 (6) Polyox WSR N-750 available from Amerchol
 (7) Polyox WSR N-3000 available from Amerchol
 (8) Polyox WSR N-60K available from Amerchol
 (9) Viscasil 330M available from General Electric Silicones
 (10) DC1684 available from Dow Corning Silicones
 (11) ZPT having an average particle size of about 2.5µm, available from Arch/Olin.

Shampoo Compositions - Examples 21-30

Components	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27	Example 28	Example 29	Example 30
Sodium Laureth Sulfate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Sodium Lauryl Sulfate	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Cocamidopropyl Betaine										
Sodium Cocoisethionate										
EGDS	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
CMEA	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800
Cetyl Alcohol	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600
Guar Hydroxy Propyl Trimonium Chloride (1)	0.500		0.400	0.250	0.500	0.500	0.500	0.500	0.500	0.500
Guar Hydroxy Propyl Trimonium Chloride (2)										
Guar Hydroxy Propyl Trimonium Chloride (3)										
Polyquaterium-10 (4)										
Polyquaterium-10 (5)	0.500	0.500	0.100							
PEG-7M (6)	0.100		0.100							
PEG-14M (7)										
PEG-45M (8)										
Dimethicone (9)	0.85	1.40	0.85	0.85	0.85	0.85	1.35	1.00	0.85	0.85
Dimethicone (10)										
ZPT (11)	1.00	1.00	1.00	1.00	1.00	0.50	1.00	1.00	2.00	2.00
Zinc Oxide	1.20	1.20	1.20	1.20						
Zinc Hydroxy Carbonate					1.61	1.61	1.61	1.61	1.61	0.80
Sodium Bicarbonate	0.20	0.20	0.20	0.20						
Hydrochloric Acid	0.78	0.78	0.78	0.78	0.42	0.42	0.42	0.42	0.42	0.42
Magnesium Sulfate	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Sodium Chloride	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800
Sodium Xylenesulfonate										
Perfume	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750
Sodium Benzoate	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250
Kathon	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Benzyl Alcohol	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
% Maximum XO Lability					74.0%					
% Soluble Zinc					0.022					

- (1) Guar having a molecular weight of about 400,000, and having a charge density of about 0.84 meq/g, available from Aqualon.
 (2) Guar having a molecular weight of about 400,000, and having a charge density of about 2.0 meq/g, available from Aqualon.
 (3) Cationic guar Jaguar C17 available from Rhodia
 (4) Polymer JR30M available from Amerchol
 (5) Polymer LR400 available from Amerchol
 (6) Polyox WSR N-750 available from Amerchol
 (7) Polyox WSR N-3000 available from Amerchol
 (8) Polyox WSR N-60K available from Amerchol
 (9) Viscasil 330M available from General Electric Silicones

- (10) DC1664 available from Dow Corning Silicones
 (11) ZPT having an average particle size of about 2.5µm, available from Arch/Olin.

Shampoo Compositions - Examples 31-40

Components	Example 31	Example 32	Example 33	Example 34	Example 35	Example 36	Example 37	Example 38	Example 39	Example 40
Sodium Laureth Sulfate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Sodium Lauryl Sulfate	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Cocamidopropyl Betaine										
Sodium Cocoisethionate										
EGDS	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
CMEA	0.800	0.800	1.600	0.800	0.800	1.600	0.800	0.800	0.800	0.800
Cetyl Alcohol	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600
Guar Hydroxy Propyl Trimonium Chloride (1)	0.500	0.500	0.500				0.500	0.500	0.500	0.500
Guar Hydroxy Propyl Trimonium Chloride (2)					0.500					
Guar Hydroxy Propyl Trimonium Chloride (3)				0.500		0.500				
Polyquaterium-10 (4)										
Polyquaterium-10 (5)										
PEG-7M (6)							0.200			0.100
PEG-14M (7)								0.200		
PEG-45M (8)									0.200	
Dimethicone (9)	0.85		0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
Dimethicone (10)		1.00								
ZPT (11)	2.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Zinc Oxide										
Zinc Hydroxy Carbonate	0.40	1.61	1.61	1.61	1.61	1.61	1.61	1.61	1.61	1.61
Sodium Bicarbonate										
Hydrochloric Acid	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
Magnesium Sulfate	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Sodium Chloride	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800
Sodium Xylenesulfonate										
Perfume	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750
Sodium Benzoate	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250
Kathon	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Benzyl Alcohol	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
% Maximum XO Liability			65.6%				76.2%			
% Soluble Zinc										

- (1) Guar having a molecular weight of about 400,000, and having a charge density of about 0.84 meq/g, available from Aqualon.
 (2) Guar having a molecular weight of about 400,000, and having a charge density of about 2.0 meq/g, available from Aqualon.
 (3) Cationic guar Jaguar C17 available from Rhodia
 (4) Polymer JR30M available from Amerchol
 (5) Polymer LR400 available from Amerchol
 (6) Polyox WSR N-750 available from Amerchol
 (7) Polyox WSR N-3000 available from Amerchol
 (8) Polyox WSR N-60K available from Amerchol
 (9) Viscasil 330M available from General Electric Silicones
 (10) DC1664 available from Dow Corning Silicones
 (11) ZPT having an average particle size of about 2.5µm, available from Arch/Olin.

Shampoo Compositions - Examples 41-50

Components	Example 41	Example 42	Example 43	Example 44	Example 45	Example 46	Example 47	Example 48	Example 49	Example 50
Sodium Laureth Sulfate	10.00	12.50	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Sodium Lauryl Sulfate	6.00	1.50	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Cocamidopropyl Betaine	2.00	2.70								
Sodium Cocoisethionate			2.00							
EGDS	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
CMEA	0.800	0.800	0.800	1.600	1.600	0.800	0.800	0.800	0.800	0.800
Cetyl Alcohol	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600
Guar Hydroxy Propyl Trimonium Chloride (1)	0.500	0.500	0.500	0.500						
Guar Hydroxy Propyl Trimonium Chloride (2)										
Guar Hydroxy Propyl Trimonium Chloride (3)										
Polyquaterium-10 (4)						0.500	0.500			
Polyquaterium-10 (5)					0.500			0.500	0.500	0.250
PEG-7M (6)				0.200			0.100		0.100	
PEG-14M (7)										
PEG-45M (8)										
Dimethicone (9)	0.85	0.85	0.85	0.85	1.40	1.40	1.40	1.40	0.85	0.85
Dimethicone (10)										
ZPT (11)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Zinc Oxide										
Zinc Hydroxy Carbonate	1.61	1.61	1.61	1.61	1.61	1.61	1.61	1.61	1.61	1.61
Sodium Bicarbonate										
Hydrochloric Acid	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
Magnesium Sulfate	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Sodium Chloride	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800
Sodium Xylenesulfonate										
Perfume	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750
Sodium Benzoate	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250	0.250
Kathon	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Benzyl Alcohol	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225	0.0225
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
% Maximum XO Lability	66.7%			66.9%						
% Soluble Zinc										

- (1) Guar having a molecular weight of about 400,000, and having a charge density of about 0.84 meq/g, available from Aqualon.
 (2) Guar having a molecular weight of about 400,000, and having a charge density of about 2.0 meq/g, available from Aqualon.
 (3) Cationic guar Jaguar C17 available from Rhodia
 (4) Polymer JR30M available from Amerchol
 (5) Polymer LR400 available from Amerchol
 (6) Polyox WSR N-750 available from Amerchol
 (7) Polyox WSR N-3000 available from Amerchol
 (8) Polyox WSR N-80K available from Amerchol
 (9) Viscasil 330M available from General Electric Silicones
 (10) DC1684 available from Dow Corning Silicones
 (11) ZPT having an average particle size of about 2.5µm, available from Arch/Olin.

Shampoo Compositions - Examples 51-54

Components	Example 51	Example 52	Example 53	Example 54A	Example 54B
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Sodium Laureth Sulfate	10.00	10.00	10.00	10.00	10.00
Sodium Lauryl Sulfate	6.00	6.00	6.00	6.00	6.00
Cocamidopropyl Betaine					
Sodium Cocoisethionate					
EGDS	1.50	1.50	1.50	1.50	1.50
CMEA	0.800	0.800	0.800	0.800	0.800
Cetyl Alcohol	0.600	0.600	0.600	0.600	0.600
Guar Hydroxy Propyl Trimonium Chloride (1)	0.400				0.500
Guar Hydroxy Propyl Trimonium Chloride (2)		0.500	0.500	0.500	
Guar Hydroxy Propyl Trimonium Chloride (3)					
Polyquaterium-10 (4)					
Polyquaterium-10 (5)	0.100				
PEG-7M (6)	0.100				
PEG-14M (7)					
PEG-45M (8)					
Dimethicone (9)	0.85	0.85	0.85	0.85	0.85
Dimethicone (10)					
ZPT (11)	1.00				
Zinc Oxide					
Zinc Hydroxy Carbonate	1.61	1.61	0.80	0.40	1.61
Sodium Bicarbonate					
Fumaric Acid					0.53
Hydrochloric Acid	0.42	0.42	0.42	0.42	
Magnesium Sulfate	0.28	0.28	0.28	0.28	0.28
Sodium Chloride	0.800	0.800	0.800	0.800	0.800
Sodium Xylenesulfonate					
Perfume	0.750	0.750	0.750	0.750	0.750
Sodium Benzoate	0.250	0.250	0.250	0.250	0.250
Kathon	0.0008	0.0008	0.0008	0.0008	0.0008
Benzyl Alcohol	0.0225	0.0225	0.0225	0.0225	0.0225
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
% Maximum XO Lability					
% Soluble Zinc					

- (1) Guar having a molecular weight of about 400,000, and having a charge density of about 0.84 meq/g, available from Aqualon.
(2) Guar having a molecular weight of about 400,000, and having a charge density of about 2.0 meq/g, available from Aqualon.
(3) Cationic guar Jaguar C17 available from Rhodia
(4) Polymer JR30M available from Amerchol
(5) Polymer LR400 available from Amerchol
(6) Polyox WSR N-750 available from Amerchol
(7) Polyox WSR N-3000 available from Amerchol
(8) Polyox WSR N-60K available from Amerchol
(9) Viscasil 330M available from General Electric Silicones
(10) DC1684 available from Dow Corning Silicones
(11) ZPT having an average particle size of about 2.5µm, available from Arch'Olin.

Cleansing Compositions – Examples 55-61

A suitable method for preparing the anti-microbial cleansing compositions described in Examples 55-61 (below) follows:

Components 1-3, 9, and 10 are mixed with heating to 190F. Components 4, 12, 15 and 17 are mixed at room temperature in a separate pot. After the first mixture has reached 190F, it is added to the second mixture. After this mixture has cooled below 140 F, components 13 (& 5) is added. In a separate vessel at 160 F, the petrolatum and ZnO or ZHC are mixed. When the aqueous phase has cooled below 110 F, the petrolatum/ZnO or ZHC blend is added and agitated until smooth. ZnO or ZHC can also be added to a premix of surfactants or water with or without the aid of a dispersing agent via conventional powder incorporation and mixing techniques into the cooled mixture. Adjustment of ZnO particle size can be affected by various conventional mixing techniques obvious to one skilled in the art. Finally the perfume is added.

Components	Example 55	Example 56	Example 57	Example 58	Example 59	Example 60	Example 61
1 Sodium Lauryl Sulfate	4.000	4.000	4.000	4.000	4.000	4.000	4.000
2 Sodium Laureth Sulfate	3.000	3.000	3.000	3.000	3.000	3.000	3.000
3 Sodium Laruroamphoacetate	4.000	4.000	4.000	4.000	4.000	4.000	4.000
4 Sodium Lauroyl Sarcosinate	2.000	2.000	2.000	2.000	2.000	2.000	2.000
5 Zinc Pyrithione (1)							1.000
6 Zinc Oxide treated with silicone (2)	2.000					6.000	6.000
7 Zinc Oxide		2.000			5.000		
8 Zinc Hydroxy Carbonate			2.000	4.000			
9 Lauric Acid	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10 Trihydroxystearin	0.650	0.650	0.650	0.650	0.650	0.650	0.650
11 Citric Acid	as needed	as needed	as needed	as needed	as needed	as needed	as needed
12 Sodium Benzoate	0.250	0.250	0.250	0.250	0.250	0.250	0.250
13 Glydant	0.120	0.120	0.120	0.120	0.120	0.120	0.120
14 Perfume	0.750	0.750	0.750	0.750	0.750	0.750	0.750
15 Polyquaterium-10 (3)	0.750	0.750	0.750	0.750	0.750	0.750	0.750
16 Petrolatum	15.000	15.000	15.000	15.000	15.000	15.000	15.000
17 Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.

(1) ZPT having an average particle size of about 2.5 μ m, available from Arch/Olin.

(2) Z-Cote HP-1 available from BASF

(3) Polymer JR30M available from Amerchol

Cleansing/ Facial Compositions – Examples 62-75

A suitable method for preparing the anti-microbial cleansing/ facial compositions described in Examples 62-75 are known to those skilled in the art, and may be prepared by any known or otherwise effective technique, suitable for providing an anti-microbial cleansing/ facial composition provided that the resulting composition provides the excellent anti-microbial benefits described herein. Methods for preparing the anti-microbial cleansing/ facial compositions embodiments of the present invention include

conventional formulation and mixing techniques. A method such as that described in U.S. Pat. No. 5,665,364, could be employed.

Components	Example 62	Example 63	Example 64	Example 65	Example 66	Example 67	Example 68
Cetyl Betaine	6.667	6.667	6.667	6.667	6.667	6.667	6.667
PPG-15 Stearyl Ether	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Sodium Lauryl Sulfate	3.571	3.571	3.571	3.571	3.571	3.571	3.571
Distearyldimonium Chloride							
Glycerin	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Stearyl Alcohol	2.880	2.880	2.880	2.880	2.880	2.880	2.880
Distearyldimonium Chloride	1.500	1.500	1.500	1.500	1.500	1.500	1.500
Oxidized Polyethylene	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Zinc Pyrithione (1)							1.000
Zinc Oxide	1.200		0.600		0.300		1.200
Zinc Hydroxy Carbonate		1.610		0.800		0.400	
Cetyl Alcohol	0.800	0.800	0.800	0.800	0.800	0.800	0.800
Stearth-21	0.500	0.500	0.500	0.500	0.500	0.500	0.500
Behenyl Alcohol	0.320	0.320	0.320	0.320	0.320	0.320	0.320
PPG-30	0.250	0.250	0.250	0.250	0.250	0.250	0.250
Stearth-2	0.250	0.250	0.250	0.250	0.250	0.250	0.250
Perfume	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Citric Acid	As Needed	As Needed	As Needed	As Needed	As Needed	As Needed	As Needed
Sodium Citrate	As Needed	As Needed	As Needed	As Needed	As Needed	As Needed	As Needed
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
Components	Example 69	Example 70	Example 71	Example 72	Example 73	Example 74	Example 75
Sodium Laureth Sulfate	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Disodium Cocamphodiacetate	7.000	7.000	7.000	7.000	7.000	7.000	7.000
PEG-80 Glyceryl Cocoate	3.500	3.500	3.500	3.500	3.500	3.500	3.500
Sodium Chloride	2.170	2.170	2.170	2.170	2.170	2.170	2.170
Glycol Distearate	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Zinc Pyrithione (1)							1.000
Zinc Oxide	1.200		0.600		0.300		1.200
Zinc Hydroxy Carbonate		1.610		0.800		0.400	
Dimethicone	0.900	0.900	0.900	0.900	0.900	0.900	0.900
Sodium Trideceth-7 Carboxylate	0.502	0.502	0.502	0.502	0.502	0.502	0.502
Perfume	0.320	0.320	0.320	0.320	0.320	0.320	0.320
Citric Acid	As needed	As needed	As needed	As needed	As needed	As needed	As needed
Quaternium-15	0.150	0.150	0.150	0.150	0.150	0.150	0.150
Polyquaternium-10	0.150	0.150	0.150	0.150	0.150	0.150	0.150
PEG-30 Glyceryl Cocoate	As Needed	As Needed	As Needed	As Needed	As Needed	As Needed	As Needed
Water	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.

(1) ZPT having an average particle size of about 2.5µm, available from ArchOlin.

10. Other Ingredients

The present invention may, in some embodiments, further comprise additional optional components known or otherwise effective for use in hair care or personal care products. The concentration of such optional ingredients generally ranges from zero to about 25%, more typically from about 0.05% to about 20%, even more typically from about 0.1% to about 15%, by weight of the composition. Such optional components should also be physically and chemically compatible with the essential components described herein, and should not otherwise unduly impair product stability, aesthetics or performance.

Non-limiting examples of optional components for use in the present invention include anti-static agents, foam boosters, anti-dandruff agents in addition to the anti-dandruff agents described above, viscosity adjusting agents and thickeners, suspension materials (e.g. EGDS, thixins), pH adjusting agents (e.g. sodium citrate, citric acid, succinic acid, sodium succinate, sodium maleate, sodium glycolate, malic acid, glycolic acid, hydrochloric acid, sulfuric acid, sodium bicarbonate, sodium hydroxide, and sodium carbonate), preservatives (e.g. DMDM hydantoin), anti-microbial agents (e.g. triclosan or triclocarbon), dyes, organic solvents or diluents, pearlescent aids, perfumes, fatty alcohols, proteins, skin active agents, sunscreens, vitamins (such as retinoids including retinyl propionate, vitamin E such as tocopherol acetate, panthenol, and vitamin B3 compounds including niacinamide), emulsifiers, volatile carriers, select stability actives, styling polymers, organic styling polymers, silicone-grafted styling polymers, cationic spreading agents, pediculocides, foam boosters, viscosity modifiers and thickeners, polyalkylene glycols and combinations thereof.

Optional anti-static agents such as water-insoluble cationic surfactants may be used, typically in concentrations ranging from about 0.1% to about 5%, by weight of the composition. Such anti-static agents should not unduly interfere with the in-use performance and end-benefits of the anti-microbial composition; particularly, the anti-static agent should not interfere with the anionic surfactant. A specific non-limiting example of a suitable anti-static agents is tricetyl methyl ammonium chloride.

Optional foam boosters for use in the present invention described herein include fatty ester (e.g. C₈-C₂₂) mono- and di (C₁-C₅, especially C₁-C₃) alkanol amides. Specific non-limiting examples of such foam boosters include coconut monoethanolamide, coconut diethanolamide, and mixtures thereof.

Optional viscosity modifiers and thickeners may be used, typically in amounts effective for the anti-microbial compositions of the present invention to generally have an

overall viscosity from about 1,000 csk to about 20,000 csk, preferably from about 3,000 csk to about 10,000 csk. Specific non-limiting examples of such viscosity modifiers and thickeners include: sodium chloride, sodium sulfate, and mixtures thereof.

O. Other Preferred Embodiments

Other preferred embodiments of the present invention include the following:

An embodiment of the present invention relates to a composition comprising 5% to 50% of a surfactant, an effective amount of a zinc containing material and from 40% to 95% water. Preferably the zinc containing material in having an aqueous solubility within the composition of less than about 25% by weight at 25°C. Preferably the zinc containing material for such a composition is an inorganic material, natural zinc containing material, ore, mineral, organic salt, polymeric salt, physically adsorbed form material, or mixtures thereof. Preferably the inorganic material in such a composition is a zinc aluminate, zinc carbonate, zinc oxide, calamine, zinc phosphate, zinc selenide, zinc sulfide, zinc silicate, zinc silicofluoride, zinc borate, or zinc hydroxide, zinc hydroxy sulfate, or mixtures thereof. Preferably the surfactant in such a composition is anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, or mixtures thereof; more preferably a mixture of an anionic surfactant and a zwitterionic surfactant, or anionic surfactant and amphoteric surfactant.

Another embodiment of the present invention relates to a composition comprising from about 5% to about 50% of a surfactant; from about 0.001% to about 10% of zinc oxide; and a ZIM; wherein the pH of the composition is greater than about 7; and wherein the ZIM is a zinc ionophore, hydrophobic zinc material, or mixtures thereof. Another embodiment of the present invention relates to a composition comprising from about 5% to about 50% of a surfactant; from about 0.001% to about 10% of zinc hydroxycarbonate, and a ZIM; wherein the pH of the composition is greater than about 7; and wherein the ZIM is a zinc ionophore, hydrophobic zinc material, or mixtures thereof. Preferably the ZIM in such a composition is a polyvalent metal salt of pyrithione, dithiocarbamate, heterocyclic amine, nonsteroidal anti-inflammatory compound, naturally occurring material having zinc ionophoric behavior, derivative of a naturally occurring material having zinc ionophoric behavior, bio-molecule, peptide, sulfur-based compound, transport enhancer, or mixtures thereof; more preferably a pyrithione or a zinc salt of pyrithione; more preferably still, zinc pyrithione. The pH of such a composition is preferably from about 7.0 to 9. Preferably such a composition comprises a compound having a having a Log zinc binding constant of less than about

6; preferably such a compound is an organic acid, strong mineral acid, zinc coordinating species, or mixtures thereof; more preferably the compound is sodium bicarbonate. Preferably the surfactant in such a composition is anionic, cationic, nonionic, amphoteric, zwitterionic, or mixtures thereof. Preferably the zinc containing material is present in such a composition in an amount of 0.1% to about 3% by weight of the composition. Preferably such a composition further comprises a conditioning agent. Preferably such a composition further comprises a cationic deposition polymer.

In a preferred embodiment, the zinc containing material has a aqueous solubility within a composition of less than about 25% by weight at 25°C.

In another embodiment of the present invention, the composition embodiment may be employed to treat a variety of conditions, including: athlete's foot, microbial infections, improving the appearance of a scalp, treating fungal infections, treating dandruff, treating diaper dermatitis and candidiasis, treating tinea capitis, treating yeast infections, treating onychomycosis. Preferably such conditions are treated by applying a composition of the present invention to the affected area.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

7. The composition according to any of the preceding claims wherein the zinc-containing layered material is selected from the group consisting of basic zinc carbonate hydroxide, zinc copper carbonate, copper zinc carbonate hydroxide, phyllosilicate containing zinc ions, layered double hydroxide, hydroxy double salts and mixtures thereof, preferably, wherein the zinc-containing layered material is selected from the group consisting of zinc hydroxycarbonate, hydrozincite, basic zinc carbonate and mixtures thereof.
8. The composition according to any of the preceding claims wherein the zinc-containing layered material is hydrozincite or basic zinc carbonate.
9. The composition according to any of the preceding claims wherein the zinc-containing layered material is selected from the group consisting of materials formed synthetically, materials formed in situ in a composition, or materials formed during the production process.
10. The composition according to any of the preceding claims wherein the zinc containing material has a relative zinc liability of greater than 20%, preferably wherein the zinc containing material has a relative zinc liability of greater than 25%.
11. The composition according to any of the preceding claims wherein the surfactant is selected from the group consisting of anionic, cationic, nonionic, amphoteric or zwitterionic surfactants and mixtures thereof, preferably wherein the surfactant is a mixture of an anionic surfactant and a zwitterionic or amphoteric surfactant, more preferably wherein the surfactant is an anionic surfactant.
12. A composition comprising:
 - a. an effective amount of a zinc containing material having an aqueous solubility within the composition of less than 25% by weight at 25°C;
 - b. from 5% to 50% of a surfactant; and

- c. from 0.1% to 5% of a zinc ionophoric material;
 - d. from 40% to 95% water; and
- wherein the pH of the composition is greater than 7.

13. A composition according to Claim 12 wherein the zinc containing material has a relative lability of greater than 15%.
14. The composition according to Claim 12 wherein the zinc ionophoric material is selected from the group consisting of polyvalent metal salts of pyrithiones, dithiocarbamates, heterocyclic amines, nonsteroidal anti-inflammatory compounds, naturally occurring materials having zinc ionophoric behavior, and derivatives thereof, bio-molecules and peptides, sulfur-based compounds, transport enhancers and mixtures thereof, preferably wherein the zinc ionophoric material is pyrithione or a zinc salt of pyrithione, more preferably wherein the zinc ionophoric material is zinc pyrithione.
15. The composition according to Claim 12 wherein composition comprises from 0.001% to 10% of the zinc containing material.
16. The composition according to Claim 15 wherein the zinc containing material is selected from the group consisting of inorganic materials, natural zinc containing materials, ores, minerals, organic salts, polymeric salts, or physically adsorbed form material and mixtures thereof.
17. The composition according to Claim 16 wherein the inorganic material is selected from the group consisting of zinc aluminate, zinc carbonate, zinc oxide, calamine, zinc phosphate, zinc selenide, zinc sulfide, zinc silicates, zinc silicofluoride, zinc borate, or zinc hydroxide and zinc hydroxy sulfate, zinc-containing layered material and mixtures thereof, preferably wherein the inorganic material is zinc oxide.
18. The composition according to Claim 12 wherein the composition further comprises a component selected from the group consisting of sodium bicarbonate, sources of carbonate anions and mixtures thereof.

19. The composition according to Claim 12 wherein the composition further comprises a compound having a Log zinc binding constant of less than 6, preferably wherein the Log zinc binding constant is less than 5, more preferably wherein the Log zinc binding constant is less than 4.
20. The composition according to Claim 17 wherein the zinc-containing layered material is selected from the group consisting of basic zinc carbonate hydroxide, zinc copper carbonate, copper zinc carbonate hydroxide, phyllosilicate containing zinc ions, layered double hydroxide, hydroxy double salts and mixtures thereof, preferably wherein the zinc-containing layered material is selected from the group consisting of zinc hydroxycarbonate, hydrozincite, basic zinc carbonate and mixtures thereof, more preferably wherein the zinc-containing layered material is hydrozincite or basic zinc carbonate.
21. The composition according to Claim 12 wherein the zinc containing material has a relative zinc lability of greater than 20 %, preferably wherein the zinc containing material has a relative zinc lability of greater than 25%
22. A composition comprising:
 - a. an effective amount of a zinc containing material having an aqueous solubility within the composition of less than 25% by weight at 25°C;
 - b. from 5% to 50% of a surfactant;
 - c. from 0.1% to 10% of a suspending agent;
 - d. from 40% to 95% water; andwherein the pH of the composition is greater than 7.
23. A composition according to Claim 22 wherein the suspending agent is selected from the group consisting of crystalline suspending agents, polymeric suspending agents or mixtures thereof, preferably wherein the suspending agent is a crystalline suspending agent.

24. The composition according to any of the preceding claims wherein the composition further comprises a conditioning agent.
25. The composition according to any of the preceding claims wherein the composition further comprises a cationic deposition polymer.
26. The composition according to any of the preceding claims wherein the zinc containing material has a particle size of from 100 nm to 30 μ m.
27. A method of treating microbial infections comprising the use of the composition according to any of the preceding claims.
28. A method of treating fungal infections comprising the use of the composition according to any of the preceding claims.
29. A method of treating dandruff comprising the use of the composition according to any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/08478

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 A61K31/315 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, EMBASE, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 227 156 A (WIESE ROBERT S) 13 July 1993 (1993-07-13) column 3, line 64 - line 66; claims 1,5,9; examples 2-C	1-4,6, 10-17, 19, 21-24, 27-29
Y		1,3-5
X	WO 01 00151 A (ARCH CHEM INC ;PROCTER & GAMBLE (US)) 4 January 2001 (2001-01-04) page 5, line 25 -page 6, line 19; claim 6 page 7, line 4 - line 9 page 4, line 26 - line 29 page 4, line 4 - line 8 -/--	1-4, 10-17, 21,26-29

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *A* document member of the same patent family

Date of the actual completion of the international search

11 July 2003

Date of mailing of the international search report

24/07/2003

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Pregetter, M

INTERNATIONAL SEARCH REPORT

International Publication No.

PCT/US 03/08478

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	page 4, line 55 - line 58; claims 1,5,6 ---	
X	WO 96 25913 A (UNILEVER PLC ;UNILEVER NV (NL)) 29 August 1996 (1996-08-29) page 2, line 3 -page 3, line 8 page 8, line 1 - line 4; claims 1-7; example 4 ---	1-11,27
X	US 4 161 526 A (GORMAN WILLIAM G) 17 July 1979 (1979-07-17) claims 1,2,4; example ---	1-4, 10-17, 21-24, 27-29
A	DATABASE WPI Section Ch, Week 197737 Derwent Publications Ltd., London, GB; Class B03, AN 1977-65846Y XP002247346 & JP 52 092881 A (NONOGAWA SHOJI KK), 4 August 1977 (1977-08-04) abstract -----	

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 03 08478

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.1

Although claims 27-29 are directed to a method of treatment of the human/animal body, the search has been carried out and based on the alleged effects of the compound/composition.

Continuation of Box I.1

Although claims 27-29 are directed to a method of treatment of the human/animal body, the search has been carried out and based on the alleged effects of the compound/composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/08478

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
see FURTHER INFORMATION sheet PCT/ISA/210
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/08478

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